Artists´ Pigments

A Handbook of Their History and Characteristics

VOLUME 2

ASHOK ROY, Editor



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Publisher's Note

As a result of demand, this volume of *Artists' Pigments* is reissued without modification in the form first published in 1993. For later developments and research in the field, the reader is advised to consult the newer literature on the subject.

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Preface

For decades, scholars in the museum field have looked forward to the publication of a comprehensive source on artists' materials. It was the vision of the late Rutherford J. Gettens, then of the Freer Gallery of Art, to produce an inclusive series on painters' materials based on sound research by the best scholars in the international arena. What evolved from that vision is the present series of publications on artists' pigments.

The publication in 1985 of *Artists' Pigments*, volume one, edited by Robert L. Feller, inaugurated the first step toward providing artists, conservators, scientists, and art historians with a contemporary, comprehensive publication on the history, analyses, properties, and occurrences of artists' pigments.

The National Gallery of Art is indebted to the International Institute for Conservation of Historic and Artistic Works (IIC) and its commitment to Gettens' vision. Their support and guidance have been valuable in research in the conservation field, as shown by the initial monographs in *Studies in Conservation*. The Conservation Division of the National Gallery of Art, under the supervision of Ross M. Merrill, chief of conservation, has developed and implemented a program-for the ongoing study of pigments and the publication of this series of books, the fruition of investigation and research by scientists and scholars of international standing. Even as volume two is being introduced, plans are presently underway for the publication of volume three and research on volume four.

Ashok Roy of the National Gallery, London, has exhibited exceptional skill in incorporating the latest information into the nine articles initially published in *Studies in Con-*

servation. This has been a demanding project commanding Dr. Roy's unique knowledge and considerable effort, as the original articles required extensive editing and revision to consolidate them into a coherent volume. The National Gallery of Art is additionally grateful to all of the authors for allowing us to use their manuscripts. J. Carter Brown initiated this series on artists' pigments and we are indebted to him for his support.

Funding for volume two has been generously provided by the Andrew W. Mellon Foundation. We thank the Foundation for its support, which has enabled the National Gallery of Art to implement research and educational projects important to the preservation of cultural objects housed in museums around the world.

EARL A. POWELL III
Director, National Gallery of Art

Foreword

As Rutherford J. Gettens and George Stout searched the literature in preparation for their 1943 publication, *Painting* Materials: A Short Encyclopedia, they quickly realized the lack of reliable references for artists' pigments. As early as 1958 John Gettens suggested an international cooperative venture to prepare a handbook of fifty to seventy-five pigments. From that point on, Gettens dedicated much of his time and energy to a handbook on artists' pigments and related materials. Although other books have described the painter's materials, none were the scholarly publication he envisioned. Gettens wanted a handbook of pigments, binding media, and support materials, but unlike the Encyclopedia, the handbook was to include well-defined procedures for confirming the identification of the pigments as well as concise scientific descriptions. Recognizing that a handbook encompassing all of the painters' materials was beyond a reasonable scope, a plan was developed with the International Institute for Conservation of Historic and Artistic Works. A series of pigment monographs was to be published in the IIC journal, Studies in Conservation. The monographs were to be accumulated as chapters in the handbook, publishing ten pigments in each volume. Insisting upon no compromises in the quality of research or production, Gettens established a high standard in the monographs published by IIC. Between 1966 and 1974 nine pigment monographs were published in Studies, which form the basis for the chapters in this volume.

The extensive editing and necessary color reproductions of the monographs taxed the limited financial resources of the IIC. Indeed, Gettens was becoming impatient with the slow pace of journal publications. Hoping to expedite the

monographs in book form, Gettens appealed to the National Gallery of Art to assume the burden of the project.

When J. Carter Brown, then the Gallery's newly appointed director, met with Gettens in 1971, he immediately recognized the importance of the pigment handbook and committed the support of the Gallery. The lack of a formal publication agreement and Gettens' death in 1974 stymied progress on the publication of the monographs as part of the pigment series.

The resources of the National Gallery of Art were ideal for augmentation of the pigment series and the NGA pursued the project under the leadership of Robert L. Feller, then director of the National Gallery of Art Research Project. Work on the project continued with the cooperation of international authors who produced an additional ten pigment studies. Discussions with the President of IIC, Garry Thomson, and other members of the IIC Council resulted in an agreement for the publication of the first nine pigment monographs; however, with the passing of time the original monographs published in Studies in Conservation were in need of revision and updating. The enormous task of updating and revising the original IIC monographs was accepted in 1985 by Ashok Roy of the National Gallery, London. Although this volume contains what is chronologically the first group of pigment monographs published in Studies in Conservation, the necessary delay to permit the update of the articles has resulted in their becoming volume two of the series. In recognition of the chronological history of the series, it was decided that in this volume the nine monographs from Studies published between 1966 and 1974 would be included, the original articles produced under Gettens' leadership.

With the impetus of Gettens' inspiration for the pigment handbook series, we remain indebted to him for his vision and perseverance. This project represents untold resources of professional time and expertise on behalf of the authors and editors. A project of this magnitude would not be possible without the commitment and cooperation of innumerable individuals.

This realization of this volume is due to the patience and astute skill of its editor, Ashok Roy, and the assistance of Janice Gruver of the Conservation Division, National Gallery of Art. The difficulty of locating the original illustrations, revising the monographs to conform to the artists' pigments series, and incorporating additional information

obtained using new technology, created an enormous task for the editor. Dr. Roy has provided numerous new photographs and references. The patience he has devoted to this volume makes him the worthy successor to John Gettens. This volume has been made possible by support from the Andrew W. Mellon Foundation and the Publication Fund of the National Gallery of Art.

> ROSS M. MERRILL Chief of Conservation, National Gallery of Art

Introduction

It is more than twenty years since the first two monograph articles in a series under the general title "Identification of the Materials of Paintings" were first published in Studies in Conservation, the journal of the International Institute for Conservation. At the IIC Congress in Rome in 1961, Rutherford J. Gettens and Joyce Plesters proposed that a collection of monograph articles should be assembled to form eventually "a modern handbook on the materials of painting which could serve chemists, conservators, curators, and collectors in the field of art." Ross Merrill has explained in his foreword that under John Gettens' series editorship, nine pigment monograph articles initially appeared in Studies in Conservation between 1966 and 1974. The pigments discussed represent many of the most significant and widespread inorganic color materials used throughout our cultural history, and each chapter has been written by leading international specialists in the study of artists' pigments. The plan to collect these articles together and republish them has been finally realized in this volume through the generosity and commitment of the National Gallery of Art in Washington.

The reader may know that conservation research and the technical study of artists' materials has expanded and progressed rapidly since the 1960s when this series was first outlined. It was therefore agreed between the Council of the IIC and the National Gallery of Art in Washington that it would be the most fitting tribute to John Gettens to republish the original articles in a revised and extended form to reflect new developments in all aspects of the history, investigation, and identification of artists' pigments. In undertaking this task, I have tried to keep to the spirit of the authors'

original writing. No rigidly uniform framework has been imposed in republishing the material in book form, although for each pigment the essential information relating to structure, properties, identification, and history of use has been included and often expanded from the monographs as they were first published.

In their revised form, the chapters in this book present new information for each of the pigments covered, providing a survey incorporating the newer literature. In particular, it has been possible to include more recent x-ray crystallographic data, since identification using x-ray diffraction remains an important method for many pigments. Infrared and Raman spectroscopic results have been introduced or expanded to reflect the increasing role of vibrational spectroscopy in pigment characterization, particularly with the increasing availability of Fourier transform infrared spectrometers and the potentially powerful technique offered by the Raman microprobe for small-particle analysis. The results of recent color measurements on many of the pigments have been incorporated. Scanning electron microscopy (SEM) has also seen a greatly increased application to the study of the materials of painting, not only in the powerful analytical capabilities of energy- and wavelength-dispersive x-ray spectrometers now routinely attached to the SEM, but also in the capacity for detailed examination of pigment particle morphology, outstripping both the resolving power and depth of field available with the optical microscope. It has now been possible to add many new SEM-micrographs of standard pigment specimens, revealing sometimes unexpected fine-structure in the particles examined. For example, the great variety of particle forms of verdigris (basic and neutral copper acetates) is recorded here for the first time, as well as subtle differences in the sublimed and wetprecipitated types of vermilion, previously rather difficult to distinguish by other methods. The distinction in particle characteristics shown by SEM between the two varieties of lead-tin yellow, first described by Hermann Kühn in 1968, may similarly provide a method of identification based on the smallest of possible samples. Work in this field is certain to continue to expand.

The monograph articles in their original form were remarkable for their fusion of historical documentary information and modern chemical understanding. Identifications of materials from works of art of known authorship, date, or provenance were compared with evidence from the early

technical literature, particularly treatises on painting. This approach provided a unique view of the development of artists' materials, the two aspects of the study doing much to enrich one another. For some of the pigments discussed here, significant new reference has been made to the historical literature, particularly for copper resinate, where previously only seventeenth-century recipes had been cited, and for lead—tin yellow, which can now be more decisively linked to the early technologies of the ceramics and glass industries. Research into painting treatises and manuscript sources relating to painting technologies and practices is still also an active area and can be expected in the future to contribute further to our understanding of these materials and their history of use.

Many conservators, art historians, and scientists engaged in the study of the technical history of painting have found value in the tables of "Notable Occurrences" compiled for the traditional pigments covered by this volume. These, too, have been significantly expanded, both by reference to the modern literature of the subject as surveyed in *Art and Archaeology Technical Abstracts* (AATA), and also by including many recent examples recorded in the Scientific Department of the National Gallery in London, where the techniques of European painting are regularly studied. Efforts have also been made to cite interesting examples from works in public collections elsewhere and from objects other than paintings, in accord with John Gettens' original plan for the series of monographs.

It would be misleading to suggest that all aspects of our knowledge of the group of pigments discussed here is now complete. There is research still to be done. Several of these traditional painting materials present further cases for study, both in their chemistry and in the historical record. It was not until an application of molecular orbital theory in 1976 that an explanation of the origin of color in ultramarine became possible, although there is still no totally reliable method for distinguishing natural from synthetic ultramarine in certain difficult samples. More is now known about the history of use of both mineral and artificial forms of azurite, but the chemistry behind the discoloration of the pigment in particular circumstances awaits fuller clarification. This can also be said to apply to the detailed mechanisms of blackening of lead white and of vermilion, as well as the complex chemistry behind the darkening of copper resinate paint films. There is scope for useful research into

the origin and history of use of lead—tin yellow in its two crystallographic modifications, and particularly into the relationship of the pigment to lead-based antimonal yellows (Naples yellows)—comprehensively discussed by Ian Wainwright et al. in volume one of this series. Smalt, too, remains somewhat obscure in its date of introduction in Europe; most occurrences are from the sixteenth century onwards, but with a few isolated identifications noted for fifteenth-century works. Once more the precise mechanism by which smalt discolors in oil medium requires further attention. The routine analysis of true copper resinate by modern methods such as mass spectrometry remains uncommon, while the identification of the variety of verdigris pigments and the more exotic artificial copper greens is still in its infancy for real paint samples.

Where appropriate and where possible, the majority of the illustrations from the original monograph articles have been reprinted here. A few could no longer be traced, but in all cases replacements are included. We have been fortunate to have been able to extend considerably the number of illustrations, many in color, to assist readers in their understanding and enjoyment of the subject.

Acknowledgments

The pigment monograph papers commissioned by Rutherford J. Gettens were the product of an international collaboration between conservators and conservation scientists.

Work on collecting the articles together, and their revision, has similarly relied on the generous cooperation of a number of individuals, whom I would like properly to acknowledge here. In this, two colleagues in the United States deserve special mention.

My thanks must go first to Ross Merrill, chief of conservation at the National Gallery of Art in Washington, whose plan it was to put life back into a project that had lain dormant for some years. Without his support and energetic commitment to this book it could not have appeared at all. I would like secondly particularly to thank Elisabeth West FitzHugh of the Department of Conservation and Scientific Research, Freer Gallery of Art and Arthur M. Sackler Gallery, Smithsonian Institution. She is not only a co-author with Rutherford J. Gettens of three of the chapters in this book, but she has also most kindly and meticulously assembled a great many of the original illustrations, as well as

provided a number of improved x-ray powder patterns for publication.

I owe a considerable debt to a number of other people who have contributed their help, advice, and above all information to enable this collection of articles to be published as a book. I hope they will accept my mention of them here as an appreciation of their generosity: Barbara Berrie, Ian Bristow, Nicholas Eastaugh, Bob Feller, Hermann Kühn, Peter Mactaggart, John Mills, Bruno Mühlethaler, Joyce Plesters, David Saunders, Janet Douglas, Ruth Simmons, Michael Skalka, Perry Smith, Garry Thomson, Ian Wainwright, and Peter Winsor.

Last, but by no means least, my thanks go to Janice Gruver for her tirelessly conscientious editorial efforts and for her management of the publication of this book.

> ASHOK ROY Scientific Department The National Gallery, London

Note to the reader:

Magnifications given are actual magnifications on the printed page.

Throughout this publication certain commercial materials are cited in order to specify accurately the particular experimental procedures that have been employed. Such identification does not imply recommendation or endorsement by the authors or the publisher nor does it imply that the products identified are necessarily the best available.

1

Azurite and Blue Verditer

RUTHERFORD J. GETTENS and ELISABETH WEST FITZHUGH

Current Terminology

English: azurite French: azurite German: Azurit Italian: azzurrite Spanish: azurita

Obsolete Terminology and Synonyms

German: Mountain blue, Bergblau; French: bleu de montagne, bleu d'Allemagne; Italian: azzurro della magna. (Pliny) lapis armenius; (Agricola) Berglasur; azurium citramarinum (in contrast to azurium ultramarinum).

It is listed in the *Colour Index* as CI Pigment Blue 30.

Composition and Structure

Azurite is composed of basic carbonate of copper, 2CuCO₃.Cu(OH)₂.

X-ray crystallographic studies have shown the coordination of copper in azurite to be essentially a distorted square plane, with a fifth nearest neighbor lying perpendicular to the plane (4 + 1 coordination) (Handbook of Geochemistry, n.d.).

RUTHERFORD J. GETTENS, at the time of his death in 1974, he was research consultant, Freer Gallery of Art, Smithsonian Institution, Washington.

ELISABETH WEST FITZHUGH, research associate, Freer Gallery of Art and Arthur M. Sackler Gallery, Smithsonian Institution, Washington.



Fig. 1 Azurite hand specimen from Copper Queen Mine, Bisbee, Arizona, Department of Mineral Sciences, Smithsonian Institution, specimen 104896.

Source

The mineral azurite, which is found in many parts of the world in the upper oxidized portions of copper ore deposits, is a natural pigment made by grinding to a powder (see fig. 1). Azurite mineral is usually associated in nature with malachite, CuCO₃.Cu(OH)₂, the green basic carbonate of copper which is even more abundant (see chapter 8).

History of Use

According to Lucas (1962), azurite may have been employed as a paint pigment as early as the Fourth Dynasty in Egypt. However, it was not widely

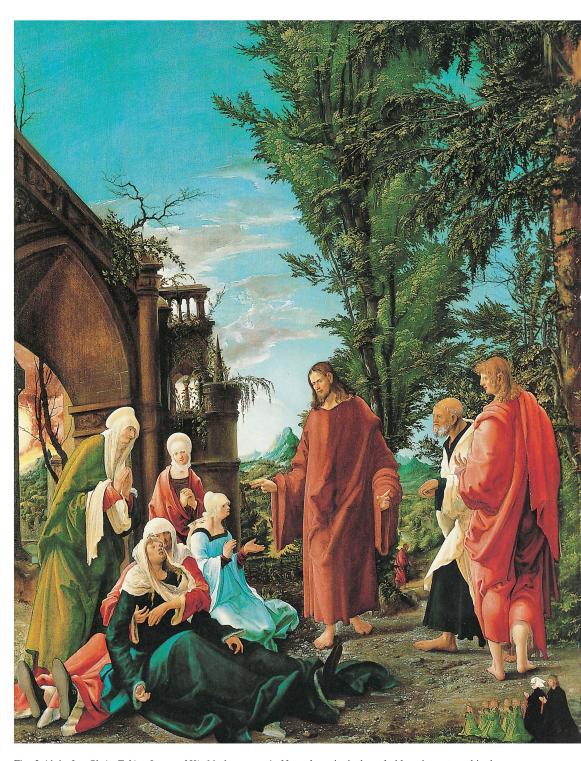
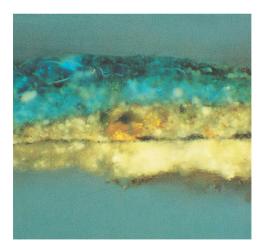


Fig. 2 Altdorfer, *Christ Taking Leave of His Mother*, panel, c.1520. National Gallery, London, No. 6463, reproduced by permission of the Trustees.

A. Natural azurite is the only blue pigment used in the composition for the draperies and, with lead white, for the sky paint.



B. Paint cross section from the hem of Mary's dark blue cloak, with natural azurite in the upper and lower layers. Reflected light, 638x. Photo: A. Roy.

used in Egypt or the classical world apparently because of the availability of the synthetic copper pigment, Egyptian blue (copper calcium silicate). Azurite was the most important blue pigment in European painting during all the Middle Ages, the Renaissance, and later (see, for example, fig. 2A and B) despite the more exotic and costly ultramarine having received greater mention. In fifteenth- and sixteenth-century European easel painting, natural azurite was commonly used as an underpaint for ultramarine (see fig. 7).

There is evidence that Hungary was the principal source of azurite in Europe until the midseventeenth century when that country was overthrown by the Turks and supplies were cut off (Laurie, 1914; Van de Graaf, 1958). This is substantiated in part by the fact that Hungary is reported as a present-day locality for azurite (Dana, 1951; Zsivny, 1948). Other sources may have been Chessy (near Lyon in France) and Sardinia, both modern localities.

Azurite was also the most important blue pigment in the paintings of the Far East. It was used widely in the wall paintings of the Sung and Ming dynasties in Central China. It was also used in Japan, especially on paintings of the Ukiyo-e School, and it is still employed by Japanese artists (fig. 3A and B). It was used to a limited extent by pre-Columbian Indians of the American Southwest and later in Spanish Mission Church paintings (Smith & Ewing, 1952).

Kühn (1973) gives a terminal date of c.1800 for

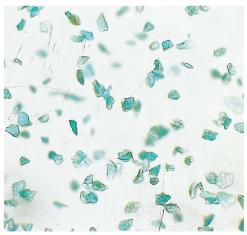
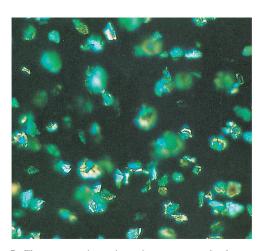


Fig. 3 Azurite (gunjo) pigment grains from a sample of modern commercial dry pigment from Japan. E. W. Forbes Collection, Fogg Art Museum, Harvard University.

A. Transmitted light, 300x.



B. The same specimen shown between crossed polars.

natural azurite in European easel painting, with the majority of occurrences before the last quarter of the seventeenth century. The invention of Prussian blue at the beginning of the eighteenth century seems largely to have displaced azurite from the palette in Europe.

Preparation

Carefully selected lump azurite needs only to be ground, washed, levigated, and sieved to prepare the pigment. Coarsely ground azurite produces dark blue; fine grinding produces a lighter tone.

The Japanese in recent times have produced three grades of azurite: coarse, medium, and fine.

Particle Characteristics

Since the pigment is made by grinding, the particles have a broken and fractured appearance (figs. 2–5); and the fracture is conchoidal. Unless well sieved, the particles are irregular in size (figs. 4 and 6), the largest often being in the 20–30 μ range. It is not uncommon to find scattered par-

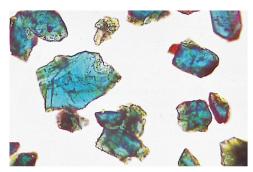
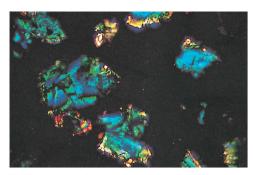


Fig. 4 Particles of mineral azurite from Simone Martini, *Madonna and Child*. Isabella Stewart Gardner Museum, Boston.

A. Bright field, 270x.



B. The same specimen between crossed polars.

ticles of malachite and cuprite because of the close association of the three minerals in nature. The proportion of these impurities strongly influences the color of an azurite paint film.

Azurite's specific gravity is 3.77; its hardness is $3\frac{1}{2}-4$.

Particle size distributions in azurite films from Early Netherlandish paintings have been studied by Van Asperen de Boer (1974).

Optical Properties

In transmitted light, coarse particles of azurite are deep blue and the finer particles are pale blue. In contrast to ultramarine, which has a purplish undertone, azurite has a greenish undertone. The larger particles show high relief and dark edges, especially when mounted in a medium of lower refractive index such as Canada balsam or Aroclor. Azurite, a monoclinic crystal, is moderately highly refracting and strongly birefracting. It is biaxial positive; refractive indices are: $\alpha = 1.730$; $\beta = 1.758$; $\gamma = 1.838$ (Larsen & Berman, 1934).

Chemical Properties

Azurite is stable to light and atmosphere. It gives off water and carbon dioxide when heated to approximately 300°C or higher and turns black with the formation of cupric oxide (Simpson et al., 1964). It is unaffected by cold alkalies but turns black when warmed with them. It is readily decomposed by dilute mineral acids with the evolu-

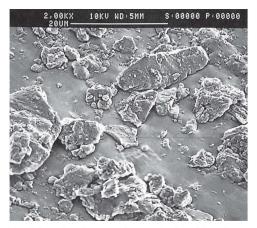


Fig. 5 Scanning electron micrograph of particles of natural azurite. Gold-coated, printed at 1,280x. Photo: A. Roy.

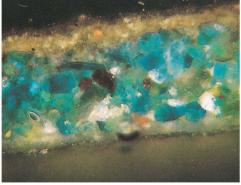


Fig. 6 Cross section of blue paint film with azurite particles on plaster. Kariye Çamii, Istanbul, fourteenth century. Reflected light, 256x.

tion of CO₂ gas. When enveloped by an organic film (medium) or when in a small quantity, particles may dissolve without noticeable release of gas.

Permanence

Despite azurite being a carbonate, and hence sensitive to acids, it has a good record in respect to permanence where employed in oil- and tempera media. It is darkened, however, by exposure to sulfur fumes, especially where it has been used in mural paintings (Augusti, 1948). Azurite pigment is also said to turn green due to alteration to malachite, as, for example, in the Cimabue fresco paintings in the ceiling of the Upper Church of St. Francis in Assisi (Augusti, 1949). There is an isolated case of azurite possibly being transformed to the basic copper chloride mineral paratacamite (Cu₂(OH)₂Cl) under special conditions (Gettens & Stout, 1958). It is unaffected by light. According to Selim Augusti (private communication), there is hardly a medieval Italian church where azurite in mural paintings does not show evidence of being transformed to malachite. An instance of transformation of azurite to malachite on mural paintings in Romania has also been reported (Istudor, 1965; Malaguzzi-Valerj, 1970).

Frequently thick layers of azurite in oil on easel paintings have become greenish or very dark and, in some cases, almost black especially when the pigment is not mixed with any other pigment. Examples may be seen in the National Gallery, London: Zurbarán's St. Margaret (no. 1930) in the saint's blue cloak, and Gerard David's The Virgin and Child with Saints and a Donor (no. 1432) in the Madonna's robe (Wyld et al., 1979). The cause of this discoloration has not been established, and transformation to malachite does not appear to be the explanation. It may, in part, be attributed to darkening of the medium in rich, coarse-textured paint layers, despite the tendency for copper pigments to exert both a siccative and an antioxidant effect on an oil film. The formation of a thin surface coating of black cupric oxide on the particles of azurite by several hypothetical mechanisms is another possible explanation. The conversion of azurite to cupric oxide (tenorite) in an alkaline environment has recently been observed on excavated polychrome sculpture (Gutscher et al., 1989). Thickly applied azurite paint is also frequently seen to be badly wrinkled and fissured although often beneath the surface the pigment remains in good condition.

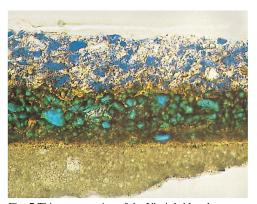


Fig. 7 Thin cross section of the Virgin's blue drapery in Dieric Bouts' *Virgin and Child*. National Gallery, London, No. 2595. The shadows of the drapery consist of a glaze of natural ultramarine over a layer of azurite, both bound in oil. Note the discoloration of the medium surrounding the azurite particles and the difference in color between the two blue pigments. Transmitted light, 630x. Photo: A. Roy.

Microchemical Tests

Ferrocyanide Test for Copper to Form Cu₂Fe(CN)₆

The test is carried out directly on the untreated sample. One drop of 5% potassium ferrocyanide (K₄Fe(CN)₆) is added to a particle of paint or scattered particles of the dry pigment so that they are completely immersed; next is added one small drop of dilute (3M) HCl. Immediately, as the acid comes in contact with the azurite particles, the released Cu2+ ions react with the surrounding ferrocyanide ions to form a gelatinous envelope of salmon-red cupric ferrocyanide. As the envelope grows, ribbons of the reddish gelatinous precipitate stream out from the central mass (fig. 8). By means of this test, copper can be detected in a single pigment particle as small as one can isolate microscopically. The sensitivity is 1.5 γ (Augusti, 1937).

Triple Nitrite Test to Form K₂PbCu(NO₂)₆

The paint sample is taken into solution with dilute nitric acid and gently evaporated to dryness. A test solution made of 0.5% lead acetate and 0.5% sodium acetate in 1% acetic acid is added to the residue. A single fragment of solid potassium nitrite is then introduced into the solution. When copper is present, it precipitates as the triple salt in the form of brown to black cubic crystals, which may be as large as $10-25\,\mu$, but are usually smaller (fig.

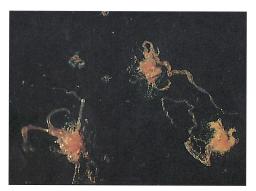


Fig. 8 Ferrocyanide test for copper showing envelopes of salmon-colored cupric ferrocyanide surrounding three separate grains of azurite. By dark field illumination. 133x.

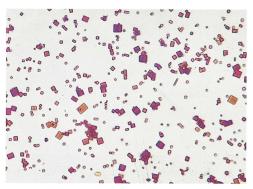


Fig. 9 Triple nitrite test for copper. By transmitted light, 400x.

9). Its sensitivity is 0.03γ (Emich, 1932). (See also Emich, 1932, pp. 83–84; Chamot and Mason, 1931, pp. 185–187.) A good photomicrograph (175x) of the crystals is shown in Wilhelm Geilmann's (1954) *Bilder zur qualitativen Mikroanalyse anorganischer Stoffe*, plate 1.

Potassium Mercuric Thiocyanate to Form Cu(SCN)₂.Hg(SCN)₂H₂O

The specimen to be tested for copper is broken down with l:3 (by volume) HCl or 1:3 HNO $_3$ and evaporated to dryness. The test reagent is prepared by adding a single crystal of potassium mercuric thiocyanate to a small drop of distilled water placed next to the residue. The residue is taken up with a drop of l:7 HNO $_3$ and the two drops are merged. Copper precipitates as greenish yellow clumps of mosslike or fernlike crystals. In dilute solutions aggregates of acicular prisms, which give parallel extinction in polarized light, are formed. The sensitivity is 0.1 γ (Augusti, 1937). Short (1940, p. 190, pl. 6), shows photomicrographs of the crystals in color; the limit of detection is 0.01% copper nitrate solution.

Spot Tests

Tests for copper in azurite using rubeanic acid (dithio-oxamide) or sodium diethyl-dithiocarbamate have been described in detail by Plesters (1956) and in Hopkin and Williams (1955). Other spot tests for copper are given by Feigl (1946). A modification of the ferric thiosulfate reaction for copper described by Feigl has been used by Hermann Kühn (private communication); the limit of detection is $0.02 \, \gamma \, \text{Cu}$.

Commercially available impregnated test papers (for example, "Cuprotesmo" test papers manufactured by Macher, Nagel and Co., Germany) may be used to detect copper at low concentrations in solution, ashed materials, and on surfaces.

Criteria for Certain Identification

Azurite can be recognized microscopically with little difficulty unless it is very finely divided. Chief diagnostic features are color, high birefringence, solubility in dilute acids, and positive test for copper by one of the tests described above. Identification of the carbonate radical is not usually necessary. See below for instrumental methods for identifying copper or the complete azurite crystal.

Emission Spectrographic Analysis

Copper is readily detected spectrographically. Prominent lines in the visible range are: 5105.54, 5153.23, and 5218.20 Å (Peterson & Jaffe, 1953); in the ultraviolet they are: 3274.0, 3247.5, and 2824.4 Å; the sensitivity is 0.0001% or better (Waring & Annell, 1953). A medium-intensity line in the spark spectrum at 2247.0 Å is also useful for the estimation of copper.

X-ray Diffraction Analysis

The three strongest lines in the x-ray diffraction powder pattern, and their respective intensities are: 5.15 (55), 3.52 (100), and 2.22 (70) Å (*JCPDS Powder Diffraction File*). Table 1 lists the

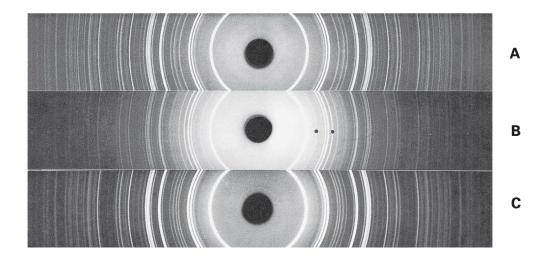


Fig. 10 X-ray diffraction powder patterns for azurite and blue verditer.

- A. Azurite mineral. Freer Gallery of Art Technical Laboratory mineral collection.
- B. Azurite. Blue pigment, Japanese painting by Utagawa Toyoharu (1735–1814), Freer Gallery of Art, No. 00.113. Quartz line marked.
- C. Blue verditer. Commercial dry pigment. Bachman & Sons.

Photographs not to be used for measurement purposes. XRD patterns by Elisabeth West FitzHugh.

spacings (d) and the intensities (I) of sample no. R8545 of azurite from the Department of Mineral Science, Smithsonian Institution, measured at the U.S. National Bureau of Standards in 1960 (Swanson et al., 1960) using filtered copper (Cu) radiation ($K\alpha$, having wavelength 1.5405 Å). Intensities are graded on a scale 1 to 100. Only twenty-one lines with intensities 10 or above are listed here; thirty-two lines with intensities below 10 are omitted (see fig. 10).

X-ray Spectrometric (X-ray Fluorescence) and Electron-Probe Microanalysis

The two chief copper lines are the $K\alpha$ line pair at c.8 keV and $K\beta$ at 8.9 keV.

Visual, Infrared, and Raman Spectrophotometry

A color reflectance curve of azurite, painted without dilution with white on rag paper with a thin parchment glue medium, published by Barnes

Table 1 X-ray Diffraction Data for Azurite^a

d (Å)	I	
∫5.15	55	
\5.08	30	
3.674	50	
3.516	100	
2.590	11	
2.540	25	
[2.523	20	
(2.510	35	
2.503	30	
2.336	17	
2.299	13	
2.287	35	
2.265	25	
2.224	70	
2.168	15	
1.948	20	
1.824	17	
1.595	15	
1.514	11	
1.477	11	
1.297	17	

a. From JCPDS Powder Diffraction File

(1939), shows a dominant wavelength of 475.6 nm, a relative brightness of 9.3%, and an excitation purity of 51.3%. A recent reflectance curve of the pigment in an acrylic medium is shown in figure 11.

Staniforth (1985) using reflectance spectrophotometry showed that excellent nonmetameric

^{11-682 (}Courtesy of JCPDS International Centre for Diffraction Data).

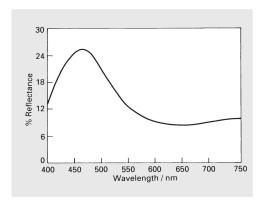


Fig. 11 Spectral reflectance curve for natural azurite in acrylic medium, 400-760 nm. CIE data: $L^*=43.29$, $a^*=-4.253$, $b^*=-21.29$. Courtesy of D. Saunders.

matches for mixtures of azurite and white may be made using the modern pigment manganese blue (barium manganate), while a fairly satisfactory match is obtained using Prussian blue.

The blue color of azurite is largely determined by a combination of d-d and charge transfer absorptions. Assignments of the crystal field transitions have been studied and compared with theoretical calculations for an essentially square planar symmetry around the copper atom (Reddy & Sarma, 1981). In the absorption spectrum, strong bands are present at 505 nm with a shoulder at 557 nm in the blue–green and at 847 nm in the infrared. A weaker d-d transition is also observed at about 607 nm.

Goldsmith and Ross (1968) examined the infrared spectrum of natural azurite and assignments

of the bands were made using normal coordinate analysis. The fundamental vibrations of the carbonate group are all observed, and these contribute strong infrared absorptions at 1490, 1415, 1090, 837, and 817 cm⁻¹, while O–H out-of-plane bending modes produce strong bands at 3425 and 952 cm⁻¹, respectively (fig. 12). Weaker bands attributable to the carbonate group may also be observed. Below 600 cm⁻¹, the copper–oxygen skeleton produces stretching bands at 495, 455, 400, 345, and 305 cm⁻¹ and bending mode absorptions at 240, 194, and 140–128 cm⁻¹. In this far region of the spectrum, the structural differences between azurite and malachite (see chapter 8) are most clearly revealed.

It has been shown recently that azurite may be identified by its Raman spectrum in a small area on a fifteenth-century illuminated book of hours. The method using the laser Raman microprobe (MOLE) requires no sample to be taken (Guineau, 1984). Prominent lines in the Raman spectrum of azurite occur at 1098, 770, 404, and 248 cm⁻¹.

In contrast to ultramarine, azurite paint films appear dark in infrared photographs and reflectograms (see figs. 11 and 12, chapter 2).

Neutron Activation Analysis

It is possible by this method to detect certain trace elements in azurite which are otherwise undetectable. Neutron activation analysis may play an important role in correlating sources of azurite mineral. Early studies indicate that parts per million of gold occur in most azurite samples. Some specimens contain parts per million of holmium; parts per 10,000 of samarium and rhenium, and parts

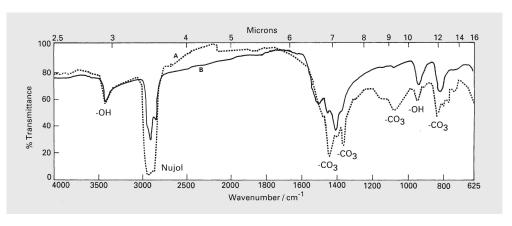


Fig. 12 Infrared absorption spectra of (a) azurite and (b) blue verditer. Nujol mulls, 4000–625 cm⁻¹.

per 1,000 of palladium and mercury. With high-resolution gamma-ray spectrometry, it should be possible to observe upwards of 10–20 trace elements in samples of the order of 1 mg or less (A. A. Gordus, Department of Chemistry, University of Michigan, private communication).

X-radiography

In the x-ray examination of paintings, areas painted with azurite show only moderate opacity to the rays. According to De Wild (1929), the mass absorption coefficient of azurite using a wavelength of 0.708 Å is 26.0; for lead white, it is 81.7; and for natural ultramarine, it is 4.0.

Ainsworth et al. (1982) demonstrated that azurite, as well as other copper pigments, produces clear autoradiographic images early in the series from the short-lived isotopes ⁶⁶Cu and ⁶⁴Cu.

Artificial Copper Blues

Blue verditer or blue bice are two of the most frequent names given to the artificial basic carbonate (of copper) of approximately the same chemical composition as azurite, although in the seventeenth century the term blue bice had been applied to the mineral pigment (Bristow, 1983). Bremen blue, cendres blue, and ashes blue are also associated with synthetic azurite. Numerous early recipes for its preparation are known (Thompson, 1936); the most straightforward of these call for the addition of calcium carbonate to copper sulfate or some other soluble copper salt. Harley (1982) gave the history of the pigment based on research into the literature. The particles may be rounded. Particle size is usually more regular than that of azurite (figs. 13 and 14), and the color is similar to that of the finely ground mineral. Peter and Ann Mactaggart (1980) have argued that in England blue verditer was a byproduct of the silver refiner's craft as a result of the chemical extraction of copper from its alloy with silver. They also prepared many specimens of both blue and green verditer (see chapter 8) under differing experimental conditions and showed that the blue basic carbonate requires precipitation at relatively low temperatures, while the green might be the more commonly formed product under less controlled conditions.

Similar microchemical tests for copper can be used. The x-ray diffraction powder data for three samples of blue verditer in the Freer Gallery Laboratory were found to be the same as for azurite.

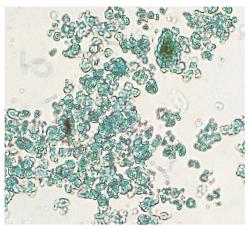
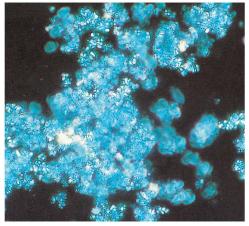


Fig. 13 Particles of blue verditer. Sample: P. Mactaggart, No. 1685. A. Bright field, 738x.



B. The same specimen between crossed polars.

These were: blue verditer (Roberson); blue verditer (Buchner & Sons, Munich, 1929); and blue verditer (Turner palette no. 20 [Hanson, 1954]).

Artificial basic copper carbonate, as "refiner's verditer," seems to have been well-established as a house-painters' color during the seventeenth century. Bristow (1983, p. 94) reports its use in 1638 for a "fair blew in Oylle" in the Dining Chamber at Ham House, Surrey, England, although the pigment was known to be best employed as a distemper paint. Despite the introduction of Prussian blue at the beginning of the eighteenth century, blue verditer continued to be used by interior decorators in both distemper and oil housepaints of light blue and for mixed greens. Some examples from English houses given by Ian Bristow (private

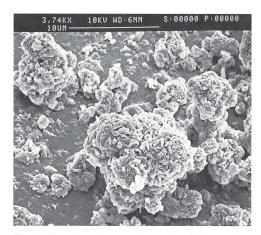
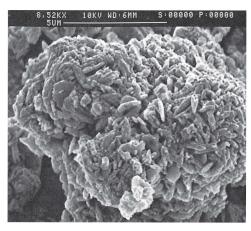


Fig. 14 Scanning electron micrographs of blue verditer, sample as fig. 13. Gold-coated. Photos: A. Roy. A. Printed at 2.394x.



B. Printed at 5,453x.

communication) are: blue verditer with yellow in distemper, to make a blue–green in the grounds of wall and ceiling panels in the Great Drawing Room at Bowood by Robert Adam, painted in 1765; in distemper for the blue papier maché border for the walls in the Breakfast Room at Osterley, c.1770, and in the oil used for cornices of the same room, probably from the 1770s; in oil to make pale green and blue on the Dining Room ceiling at Pitzhanger Manor, by George Dance the Younger, 1769; with yellow to make green on pre-1840 wallpaper found at Lauderdale House, Hammersmith, London.

Blue verditer, in conjunction with Prussian blue, was one of the pigments used in 1767/1768 to decorate the Robert Adam Drawing Room in Landsdowne House, now in the Philadelphia Museum of Art (Butler & De Florio, 1986). Butler (1982–1983) reports the use of blue verditer in several paintings by Jan Steen, in addition to the mineral pigment.

Artificial blue basic copper carbonate seems also to have been used for a variety of purposes in the decorative arts, often in combination with smalt. Peter Mactaggart (private communication) reports some examples from painted musical instruments: blue verditer mixed with smalt and indigo on the decorated soundboard and nameboard of a virginal by Philip Jones, made in London in 1671 (owned by Manchester University, at Tabley House); blue verditer combined with smalt on the arabesque borders on the soundboard of a harpsichord by Joseph Tisseran, London, 1710 (private

collection); and blue verditer mixed with smalt on the soundboard of a French harpsichord by Joannes Goermans, made in Paris, 1750 (private collection).

Notable Occurrences

Azurite has had a long and very widespread use as a pigment before the eighteenth century, and a full list of occurrences would occupy many pages. The list given below is therefore highly selective, but indicates something of the range of use. In addition to its obvious role as a blue pigment used on its own or in tint, it is often to be found in European easel painting combined in paint mixtures, particularly with yellows such as lead-tin yellow, yellow ochre, and yellow lakes to produce greens for foliage and landscapes. Sometimes the green was achieved by the use of a yellow glaze over an azurite underpaint. Similarly, azurite mixed with red lake pigments or azurite with a red lake glaze is commonly found to have been used for violet in early pictures.

- (a) Specific instances of occurrence on nineteen Dutch paintings dating from the fifteenth to midseventeenth centuries (De Wild 1929, pp. 23–24).
- (b) Mixed with lead white in the sky of the central panel of the Van Eyck altarpiece, *The Mystic Lamb*, in the Cathedral of St. Bavon, Ghent (Coremans, 1953).

- (c) In the *Retable du Saint Sacrement* by Dieric Bouts in the Église St. Pierre, Louvain (Coremans et al., 1952).
- (d) In the wall paintings of the Main Hall of the Hōryūji Temple, Japan, seventh to eighth century (Yamasaki, 1953).
- (e) On a variety of Japanese polychromed sculptures, dating from the seventh century on (Yamasaki & Nishikawa, 1970).
- (f) In the fourteenth-century wall paintings in the Byzantine Church of Our Saviour, Monastery of the Chora (Kariye Çamii), Istanbul (see fig. 6) (Gettens & Stout, 1958).
- (g) On kiva mural decorations of the pueblos of the pre-Columbian peoples of the American Southwest (Smith & Ewing, 1952).
- (h) In many Italian fresco paintings: Cimabue, Giotto, Simone Martini, Luca Signorelli, Pietro Lorenzetti. (Selim Augusti, private communication.)
- (i) On a Mexican colonial painting, *Adoration of the Magi*, by Baltasar de Echava (1580–1660), one of the important founders of the art of painting in Mexico. Painting owned by Davenport Municipal Art Gallery, acc. no. 25.84F. (Richard D. Buck, private communication.)
- (j) Mixed with lead white in the sky areas in a number of paintings by Nicolas Poussin (Delbourgo & Petit, 1960).
- (k) In a large number of paintings in the National Gallery, London. Identified by microscopy, often supplemented by microchemical tests or spectrographic analysis. Selected examples include:

Ascribed to Giotto (no. 5360), Duccio (no. 6386), Ugolino di Nerio (no. 684–6), Giovanni di Paolo (no. 3402), Piero della Francesca (no. 665), Fra Filippo Lippi (no. 3424), Filippino Lippi (no. 4905), Perugino (no. 288), Bronzino (no. 5280), Cossa (no. 597), Ercole de'Roberti (no. 1127), Giovanni Bellini (no. 726), Cima (nos. 300, 816), Titian (no. 35), Bordon, (no. 1845), Tintoretto (nos. 16, 1130, 1313, 1476, 4004), Lotto (nos. 1047, 1105, 2281), Leonardo (no. 1093), Correggio (nos. 10, 4255), Parmagianino (no. 2441).

Rogier van der Weyden (no. 654), Dieric Bouts (nos. 664, 2595), Gerard David (nos. 1078, 1070, 1432), Lucas van Leyden (no. 3604), Maarten van Heemskerck (nos. 6508a, 6508b), Peter Paul Rubens (nos. 46, 66, 194, 4815), Rembrandt (nos. 47, 4930, 6300, 6350), and Pieter de Hoogh (no. 835).

Style of Martin Schongauer (no. 723), Master of St. Bartholomew (no. 707), Master of Liesborn (no. 2153), Master of Cappenberg (no. 263), Albrecht Altdorfer (no. 6463, see fig. 2), Hans Holbein (no. 2475).

Zurbarán (no. 1930), Velázquez (no. 1378).

For picture titles and dates, see National Gallery *catalogues* (London). Reported by Joyce Plesters and Ashok Roy.

As the only blue pigment identified in the seven Raphael cartoons for tapestries (in the collection of Her Majesty the Queen, and on loan to the Victoria and Albert Museum, London), reported by Joyce Plesters (private communication).

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2

Ultramarine Blue, Natural and Artificial

JOYCE PLESTERS

Ultramarine Blue, Natural

Current Terminology

English: ultramarine (natural)
French: outremer (lapis)
German: Ultramarin (echt)
Italian: oltremare (genuino)
Spanish: ultramar (ino) (verdadero)

Obsolete Terminology and Synonyms

Az(z)ur(r)um ultramarinum, az(z)ur(r)um transmarinum, az(z)ur(r)o oltramarino, azur d'Acre, pierre d'azur, Lazurstein, lapis lazuli ultramarine (alternative spellings shown in parentheses).

Early nomenclature is complex. The name of the mineral from which the pigment is obtained, *lapis lazuli*, derives from the Latin *lapis*, a stone, and *lazulus*, a Latinized form of the Persian word for blue. The term ultramarine was originally used as an adjective, as for example in *azzurro oltramarino*, and was applied to other imported commodities. It served to distinguish the genuine lapis lazuli ultramarine, which was imported from Asia, from other blue pigments, in particular from the blue copper mineral pigment azurite, which went under the name of az(z)ur(r)o dell'Allemagna (frequently corrupted to az[z]ur[r]o citramarinum [see chapter 1]). The history of the nomenclature of ultramarine has been discussed by

Merrifield (1849), who formed the opinion that the term ultramarine must have been in use in Italy by the beginning of the fourteenth century and by Gettens (1950). Filarete (1890) wrote in 1464, "Fine blue is derived from a stone and comes from across the seas and so is called ultramarine."

Composition

A complex sulfur-containing sodium aluminum silicate, given in Dana (1971) as (Na,Ca)₈(AlSiO₄)₆(SO₄,S,Cl)₂, the proportions of aluminum (Al), silicon (Si), and oxygen (O) being fixed in an aluminosilicate framework, the other elements present as cations and anions are variable (see also Chemical Composition).

Source

The mineral, lapis lazuli, from which the pigment is made, is a complex rock mixture. Fundamentally it is a mineralized limestone containing grains of the blue cubic mineral called lazurite, which is the essential constituent of the pigment; although two isomorphous minerals of the sodium-aluminium-silicate group, haüynite and sodalite—the former containing a sulfate group and the latter, chloride-may also be present, both of which sometimes occur in a blue form as well as in a variety of other colors. Other silicate minerals, such as diopside, forsterite, muscovite, and wollastonite, are likely ingredients of lapis lazuli, while invariably present are calcite (optically active crystalline calcium carbonate) and pyrites (iron sulfide). (For further details of the mineral-

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Fig. 1 Lapis lazuli from Afghanistan. Cut and polished specimen. White veins of crystalline impurities and gold-colored flecks of pyrites are visible. British Museum (Natural History), No. BM60277.

ogy of lazurite and its associated impurities in lapis lazuli, see the supplementary notes appended to the original of this article [Plesters, 1966]).

Samples of lapis lazuli mineral differ considerably in quality and appearance. The best are of a uniform deep blue, but other specimens are of a paler color or else the blue is intermingled with white crystalline material. Characteristic of the appearance of the mineral is a scattering, or sometimes veining, of small, bright, metallicappearing golden or silver-colored particles of pyrites, likened by classical authors to stars in a blue sky, and sometimes mistaken for gold (see fig. 1). In the past, the main source of the mineral was in Asia in the ancient quarries of Badakshan (now in Afghanistan); these quarries were described by Marco Polo (Frampton & Penzer, 1937) in connection with the journey he made in 1271, and he specifically stated that the mineral was used for the extraction of a blue pigment. In earlier times, Badakshan seems to have provided practically all of the lapis lazuli used in Europe. When the traveler John Wood (1841) visited the mines in 1837, they appeared to have been out of use for several years, but an Oxford University expedition to Afghanistan (1964) ascertained that mining of lapis lazuli had, to some extent, been resumed there.

The mineral was probably imported into Europe mainly by way of Venice, the principal port for trade with the East. Some confirmation that Venice was the distribution point, and probably the chief manufacturing center for the pigment, was provided by Nicholas Hilliard, the sixteenth-century English miniaturist, who remarked that "the

darkest and highest blew is ultermaryne of Venice" (Norman, 1912). Hilliard also added, however, that its prohibitive price compelled painters to use other blues such as smalt (see chapter 5) and blue bice (artificial azurite, see chapter 1). Lapis lazuli is a comparatively rare mineral and the only other sizeable deposits appear to be near Lake Baikal in Siberia and in the Chilean Andes (Dana, 1971), neither of which was worked until the nineteenth century. There are smaller deposits in Argentina, Burma, Canada, and the United States. A comprehensive account of the early history and sources of the mineral was given by Gettens (1950). Monticelli and Covelli (1825) gave nineteenth-century accounts of deposits of the mineral in Italy, but presumably these deposits were of insufficient quantity or quality to provide a useful supply of pigment.

Preparation

Unless the mineral is of very high quality, simple grinding and washing, as carried out for the preparation of other mineral pigments, for example, azurite, produces only a pale grayish blue powder lacking in purity and depth of color. Laurie (1914) observed in Byzantine manuscripts of the sixth to the twelfth centuries that ultramarine of this description containing a high proportion of colorless material may have been prepared in this simple way.

Soon after 1200, an improved method of extraction came into use, as revealed in thirteenthcentury references (Thompson, 1936). Literary sources from the fourteenth century on contain numerous instructions, one of the most detailed being given by Cennino Cennini, writing at the beginning of the fifteenth century, but, in general, describing fourteenth-century practice (Thompson, 1933), and in the fifteenth-century Bolognese manuscript, which gives numerous versions differing only in detail (Merrifield, 1849). A full account of the Bolognese manuscript methods and other recipes recorded in the early literature have been reviewed and presented in tabular form (Kurella & Strauss, 1983). The principle of the method was that the ground mineral was incorporated into a mixture of melted wax, resins, and oils (a multiplicity of ingredients appearing to be regarded as beneficial) and the molten mass, usually wrapped in a cloth, kneaded under a dilute solution of lye (a solution of potassium carbonate prepared by extracting wood ashes with water). Blue particles of lazurite are washed out by this process and are collected by settling at the bottom of the vessel, while most of the colorless crystalline material and other impurities remain behind in the doughy mass. The effectiveness of the method probably depends on the preferential wetting of the blue particles. The largest and deepest-colored blue particles emerge first and it was usual to carry out at least three separate extractions by this means, collecting several grades of pigment of diminishing quality. The product of the last extraction, containing a high proportion of colorless material and both few and small blue particles, was known as ultramarine ash, which, because of its high degree of transparency, was valued as a pale blue glazing pigment. The traditional mode of extraction was carried out virtually unchanged into the present century. Schmidt (1847), for example, described it in his handbook of pigment preparation, by which time the manufacture of synthetic ultramarine was well underway. An interesting account of extraction carried out by Cennino's method was given by Denninger (1964). It should be noted that however carefully the extraction is carried out, some natural impurities, notably calcite, still seem to remain in the pigment, and these serve to distinguish the natural from the synthetic product (see, for example, fig. 4A and B).

History of Use

Although archaeological evidence and accounts in early literature have shown that lapis lazuli was used as a semi-precious stone and decorative building stone from early Egyptian times, and the mineral is accurately described by such classical authors as Theophrastus and Pliny, there is so far no evidence that it was used ground as a painting pigment either by the ancient Egyptians or by the Greeks and Romans (all of whom had in any case a very satisfactory blue in the synthetic copper silicate pigment, Egyptian blue, the secret of the manufacture of which subsequently was lost). The earliest occurrence of lapis lazuli used as a painting pigment was noted by Gettens (1937–1938a) in sixth- and seventh-century A.D. wall paintings in cave temples at Bāmiyān in Afghanistan, not far from the most famous source of the mineral. Laurie (1935–1936) identified it on Persian miniatures of the thirteenth and fourteenth centuries. Identifications on Chinese paintings of the tenth to eleventh centuries were made by Rutherford J. Gettens (see Notable Occurrences). Paramasivan (1937– 1938) reported finding natural ultramarine on Indian mural paintings of the eleventh, twelfth, and seventeenth centuries.

In Europe, the pigment probably found its most extensive use in the fourteenth to mid-fifteenth centuries, particularly in illuminated manuscripts and in Italian panel paintings, its jewellike brilliance complementing that of vermilion and gold. The high cost of the imported raw material and the long laborious process of extraction combined to make good-quality ultramarine as expensive as gold. Merrifield (1849) cited numerous contracts for paintings in which the use of ultramarine was specified. In many cases the patron agreed to pay for, or to supply, the ultramarine to be used just as he did the gold leaf. Haskell (1963) cited several seventeenth-century contracts of this type. In fourteenth-, fifteenth-, and sixteenth-century pictures, the highest quality and most intensely bluecolored ultramarine can often be seen to have been reserved for the robes of Christ and the Virgin (see, for example, fig. 2). The size of the picture and the status of both artist and commission seem also likely to have influenced its use. In the National Gallery, London, a small triptych by Duccio (no. 566) (fig. 11A) has the Virgin's blue cloak painted in ultramarine, whereas a large panel attributed to School of Duccio (no. 565) has the Virgin's blue cloak of the rather less costly pigment azurite (see chapter 1). Economies were sometimes effected either by underpainting with azurite, as in the blue drapery of the Virgin in Giovanni Bellini's Madonna of the Meadow (National Gallery, London, no. 599) and similarly in the central panel of an altarpiece by Perugino, The Virgin and Child (National Gallery, London, no. 288) (Bomford et al., 1980), or occasionally, as in dark blue backgrounds of late Byzantine wall paintings at Sancta Sophia, Trebizond, with carbon black (Plesters, 1963). The latter technique is also sometimes associated with polychrome sculpture, and occasionally seen in easel painting, for example in Poussin's The Adoration of the Golden Calf (National Gallery, London, no. 5597) where a layer of charcoal black underlies natural ultramarine in the shadows of a blue drapery. The other traditional blue pigments have also been found in underlayers for surface paint containing genuine ultramarine, presumably used for the same motive as azurite. For example, indigo mixed with white forms the first layer of an ultramarine sky in Francesco del Cossa's St. Vincent Ferrer (National Gallery, London, no. 597) (Smith et al., 1981), and the same technique is employed by Van Dyck for a blue drapery in



Fig. 2 Detail from Titian's Madonna and Child with Saints John the Baptist and Catherine of Alexandria, canvas, 1530s. The Madonna's robe is painted in

natural ultramarine. National Gallery, London, No. 635. Reproduced by permission of the Trustees.

Charity (National Gallery, London, no. 6494). Ultramarine over smalt (see chapter 5), both pigments mixed with white, has been found in the skies in several paintings by Claude Lorrain.

Richard D. Buck (private communication), reported the discovery during the panel transfer of a fourteenth-century Sienese painting (School of Lorenzetti, Harvard University Museums of Art collection [Fogg]) of the Virgin's ultramarine robe underpainted with green (pigment unanalyzed, but having the appearance of green earth).

In the Northern European countries, natural ultramarine appears to have been employed on a somewhat less lavish scale than in Italy. Boltz (1566) in his *Illuminirbuch* remarked that it was seldom seen in Germany. This writer has not yet identified it on the limited number of German

paintings of the fifteenth and sixteenth centuries she has examined so far, although Dürer (who had, of course, traveled in Italy and been to Venice) mentioned it as an expensive pigment in one of his letters (Rupprich, 1956). In the Early Netherlandish School, as in the German School, azurite is the more commonly encountered blue pigment, ultramarine being used as a solid layer of color usually only for the drapery of iconographically important figures in major works, such as the Van Eyck polyptych of the Adoration of the Mystic Lamb, elsewhere more often as a glaze over azurite or mixed with it (Coremans, 1954; Coremans et al., 1952; Wyld et al., 1979) (see also fig. 7, chapter 1). In the late sixteenth and the seventeenth century, it has been noted (see chapter 1) that there was a shortage of this other most valuable pigment, azurite, which must have resulted in increased demand for the already costly ultramarine. Outside Italy the situation seems to have become serious. Nicholas Hilliard's comment has already been noted (Norman, 1912) and Francisco Pacheco (1649), the Spanish painter and author, writing in 1649, said that it was not used even by wealthy painters in Spain at that time. This statement may well be an exaggeration. Nevertheless, in several Spanish paintings of the period examined by the author, there has been a marked absence of ultramarine, and indeed, only one example of its identification on a Spanish picture of this period can be quoted in the list of Notable Occurrences. Recchuito (1977), however, reported the use of small quantities of natural ultramarine in a large panel painting by El Greco, although the principal blue pigment there was found to be azurite.

In manuals of painting of all periods there are warnings against counterfeited and adulterated natural ultramarine. Its costliness would make it an obvious subject for such practices.

Although in paintings of the past the pigment is mainly to be seen unmixed with pigments of other colors except white, ultramarine's slightly violet—blue hue made it of more value for producing purple colors by mixing it with crimson rather than using the somewhat greenish toned azurite. Occasionally physical mixtures of ultramarine with a crimson-colored lake pigment such as a madder lake were used, but more often the purple color was produced by superimposed layers of either an ultramarine glaze over an opaque pink or crimson body color, or else by a crimson glaze over an opaque blue body color of ultramarine mixed with white. Examples of these techniques are given under Notable Occurrences.

Chemical Composition and Structure

The purified blue pigment extracted from lapis lazuli is essentially the mineral now designated lazurite, the approximate compositional formula of which is given above as $(Na,Ca)_8(AlSiO_4)_6$ $(SO_4,S,Cl)_2$. Chemically, it is the most complex of all the mineral pigments. Its composition was not elucidated until the early nineteenth century when the first complete quantitative analysis was carried out (on samples of the pigment extracted in the traditional manner) by Désormes and Clément (1806). Results of subsequent careful analyses by various workers gave puzzling variations in

constitutional formulas in respect to the proportions of sodium and sulfur. In 1890, Brögger and Bäckström (1891) showed that lazurite (the term by then specified for the extracted blue pigment) was a complex sulfur-containing aluminosilicate similar to sodalite and other zeolitic or ionexchange materials. Work up to the end of the nineteenth century is well summarized in a monograph by Hoffmann (1902). Meanwhile, in 1828 artificial ultramarine had been successfully synthesized (see section on artificial ultramarine), subsequently analyzed, and found to duplicate the chemical composition and structure of natural ultramarine, the relationship being summarized in papers by Doelter (1915) and Bock (1924). The next major step toward the understanding of the structure was taken when the first x-ray diffraction powder photographs were made by Jaeger (1929). He showed that all ultramarines, natural or synthetic, and irrespective of variations in color or chemical constitution, gave identical x-ray diffraction patterns (disregarding mineral impurities in the natural material), thus indicating the same crystal lattice. The crystal structure is based on a body-centered cubic lattice of 9.08 Å side (Dana, 1971). The problem of how to fit the variable constitutional formula of ultramarines into a fixed crystal lattice has exercised the ingenuity of a great many chemists and produced a vast amount of published work. Figure 3 shows the space lattice diagram of the molecule as postulated by Leschewski (1935) and his colleagues. The blue

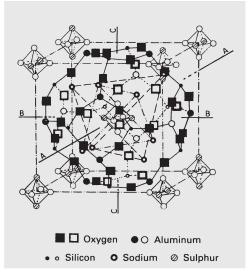


Fig. 3 The space lattice of ultramarine deduced by x-ray diffraction, according to K. Leschewski.

color, up to the nineteenth century thought to be due to the presence of iron, is now considered to be dependent on the presence of polysulfide radical ions and their location in the crystal lattice.

Lazurite is one of several rare felspathoid minerals in which the basic structure is a threedimensional basketlike framework built from aluminosilicate tetrahedra, with positive ions (principally Na+ and Ca2+) occupying the interstices. In lazurite small quantities of rubidium, caesium, or strontium may be incorporated. A diagram and a photographic stereo-pair of the structure is found in Wells (1984). In addition to the cations, anions such as Cl^- , SO_4^{2-} , and S_7^- (x = 2, 3) are essential constituents, and it is from these last entrapped species that the color of the mineral arises via anion to anion charge transfer (Nassau, 1985). Mineralogically related to lazurite are sodalite, containing chloride, and haüynite and noselite, both of which contain sulfate. Sodalite is variable in color, but is often found in a blue form.

Work by Hofmann et al. (1969) proposed the presence in ultramarine of the highly reactive radical ions S_2^- and S_3^- , which, according to molecular orbital theory, must contain unpaired electrons and are only stabilized by their occupancy of the aluminosilicate framework. The radical anions have been detected by their electron spin resonance spectra (Hofmann et al., 1969) while theoretical calculations indicate the importance of S_3^- in producing the blue color in lapis lazuli (Cotton et al., 1976).

Particle Characteristics

The blue particles are of irregular size and angular shape (as distinct from the comparatively small, uniform, and rounded grains of artificial ultramarine). Although x-ray crystallography shows lapis lazuli to be a crystalline compound, and rhombdodecahedral crystals occasionally occur in deposits of the mineral, recognizable crystalline form is rare in pigment samples, and particles are often flattish, sometimes with a conchoidal fracture. An excellent scanning electron micrograph of a single lazurite particle was published by Feller (1972). There are usually appreciable amounts of crystalline mineral impurities, mainly colorless, mixed with the blue particles. These consist chiefly of other silicate minerals (see Chemical Properties) and calcite.

Optical Properties

The particles are of a translucent pure blue by transmitted light, deep opaque blue by reflected light. The small, uniform rounded granules of the synthetic pigment appear more opaque than those of the natural pigment when viewed under the microscope, although the difference in refractive index of the two is not really significant. The refractive index is comparatively low, given by Larsen and Berman (1934) as $1.50 \pm$ and by Dana (1971) as 1.500, that is, lower than that of Canada balsam and Aroclor and only slightly higher than that of fresh linseed oil. Having a cubic crystal structure, ultramarine is isotropic, so that the blue particles (unlike those of azurite) are not birefringent, and when the pigment is examined under the polarizing microscope, they undergo complete extinction between crossed polaroids (see figs. 4B and 5B). Any calcite crystals present are, on the other hand, strongly birefringent, and as the analyzer of the polarizing microscope is rotated, those particles suitably orientated to the plane of polarization will appear as bright spots on a dark field. If occasional blue particles appear bright, this is usually traceable to overlapping with calcite particles. Two samples of natural ultramarine when viewed first by ordinary light and then with crossed polaroids are shown in figures 4 and 5. The proportion of calcite, and other mineral impurities present, varies with the quality of the mineral and the thoroughness of the extraction; but however carefully the extraction has been carried out using the traditional method, some impurities, including calcite crystals, usually seem to be present, although a particularly refined specimen of natural ultramarine has been found on a Perugino altarpiece (fig. 6) (Bomford et al., 1980). In his examination of specimens of the natural pigment taken from sixteen different Netherlandish, Dutch, and Flemish pictures dating from between 1437 and 1810, De Wild (1929) found that all contained colorless calcite particles to a greater or lesser extent. Since calcite does not occur as an impurity in the synthetic pigment, it is therefore possible to distinguish between the natural and synthetic ultramarine by means of the polarizing microscope, or by the particle form and size distributions in natural specimens (Bomford et al., 1980).

It must be pointed out, however, that it would be virtually impossible to detect a deliberate mixture of natural and synthetic pigment. Some preliminary work described by Keisch (1970) sug-

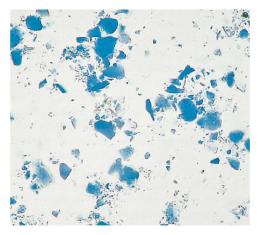


Fig. 4 Particles of natural ultramarine, Rowney's old stock.

A. Transmitted light, 615x.

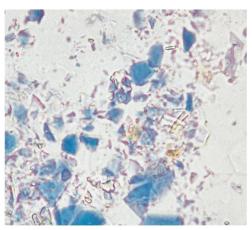
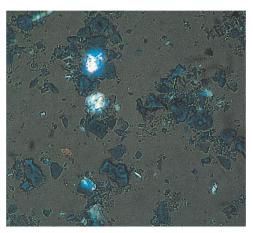
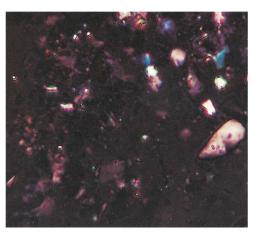


Fig. 5 Grains of natural ultramarine pigment from an illuminated Armenian MS, *The Four Gospels* (twelfth century), fol. 183 r. Freer Gallery of Art, No. 50.3. A. By transmitted light, 645x.



B. The same specimen between partially crossed polars. Certain mineral impurities associated with the lazurite, principally calcite, are strongly birefracting.



B. The same sample shown between crossed polars. 1,230x.

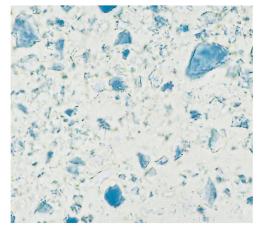


Fig. 6 Ultramarine particles from the Virgin's blue robe in an altarpiece by Perugino, *The Virgin and Child with Saints Raphael and Michael*. National Gallery, London, No. 288. Mounted in Aroclor (n=1.66). Transmitted light with oil immersion, 2,460x. Photo: A. Roy.

gesting the use of mass spectrometry to determine the sulfur isotope ratios for ³²S and ³⁴S in specimens of natural and synthetic ultramarine indicates that the two varieties may be differentiated by this means.

General Pigment Properties

The hiding power of ultramarine is rather greater than would be expected from its low refractive index, but it can be regarded as a translucent glazing color when used in oil. The tinting strength, although not comparable with, for example, modern phthalocyanine blues, is quite good—much better than that of other early blue pigments such as azurite or smalt. The distinctive pure bright blue color of the dry pigment is maintained when bound in aqueous media such as gum acacia or egg tempera, but when used alone in oil-media, on account of its low refractive index, it appears very dark blue in a thick layer (see, for example, Bomford et al., 1980). In oil it is used to best effect either mixed with a white pigment to produce a brilliant opaque blue, or else as a thin translucent glaze over a lighter underpaint.

Chemical Properties

That natural ultramarine has high stability to light is proven by the fact that examples on paintings as much as five hundred years old have as intense and pure a blue color as either the freshly extracted mineral pigment or the best synthetic pigment of similar hue. Heating to redness has no visible effect, and early in the history of the pigment this was used to distinguish the genuine material from other blue substances such as azurite, and to detect adulteration. At higher temperatures—white heat or a blow-pipe flame—ultramarine tumesces and loses its blue color, leaving a yellowish white glassy mass of silica.

The pigment is unaffected by ammonia or caustic alkalis, except on very prolonged and drastic treatment by the latter, but is very readily decomposed by acids. Dilute mineral acids—dilute HCl, HNO₃, or H₂SO₄—rapidly destroy the blue color with evolution of hydrogen sulfide gas, with a white or yellowish residue of undissolved silica remaining. Even very dilute acids will, on long standing, decolorize and decompose ultramarine, presumably because hydroxonium ions (H₃O⁺) are small enough to enter readily the open aluminosilicate framework and react with the enclosed polysulfide ions. Acetic acid attacks the pigment

rather more slowly than do mineral acids. The practice of washing lapis lazuli with vinegar, either as a preliminary to the "dough" method of extraction described above, or, as recommended in the seventeenth-century De Mayerne manuscript (Van de Graaf, 1958), as a labor-saving method of purifying the pigment, must have depended to some extent for its success on the speed and timing of the operation. Presumably the object was to dissolve some of the calcium carbonate present. In experiments carried out by this author, samples of natural ultramarine were appreciably more slowly decolorized by dilute mineral acids than were samples of synthetic pigment of similar color, but it has not yet been firmly established whether this difference might depend on the slightly coarser particle size of the natural pigment. A similar observation on the rate of attack of acids on the natural and artificial pigments was made by Church (1915).

Permanence and Compatibility with Other Pigments

On innumerable easel paintings and illuminated manuscripts, natural ultramarine can be seen in a perfect state of preservation even though it is several centuries old, and in general it behaves as a comparatively permanent pigment. Although it is a sulfur-containing compound from which sulfur is readily liberated as H₂S, in paintings of the past it was regularly mixed with lead white with no reported occurrence of blackening of the lead pigment to lead sulfide.

A disorder known as "ultramarine sickness" has occasionally been noted on paintings as a grayish or yellowish gray mottled discoloration of the paint surface, and it also occurs from time to time with artificial ultramarine used industrially. De Wild (1929) discussed the subject and felt that decomposition of the pigment is brought about in most cases by the action of atmospheric sulfur dioxide and moisture. At the same time, he suggested that acidity of an oil- or oleo-resinous paint medium might be an alternative cause and this view is shared by a number of other authorities, among them Kittel (1960). Hess (1965) attributed "ultramarine sickness" to slow drying of the oil during which time water may have been absorbed to cause swelling, opacity of the medium, and therefore whitening of the paint film. In the only example of what appeared to be "ultramarine sickness" investigated by this author-a mottled gray

discoloration on blue drapery in an oil painting by the seventeenth-century Dutch painter Karel du Jardin (National Gallery, London, no. 6296)-ultramarine particles were present in good condition in the paint film but were mixed with smalt, a blue cobalt-glass pigment which has sometimes been found to be associated with discoloration and disintegration of the oil-medium in which it has been used (see chapter 5). Hence the visible symptoms described above and generally termed "ultramarine sickness" cannot at present be assigned to a single cause. Most reported cases are on oil paintings. Assessment of the nature of discoloration should also be made with caution. In a recent investigation of Sassoferrato's The Virgin in Prayer (National Gallery, London, no. 200), the Virgin's ultramarine robe showed before cleaning the appearance of severe degradation of the blue pigment. However, after cleaning, the disturbance to the blue was found to have been entirely superficial and within later discolored retouchings and varnish layers; the original ultramarine paint layer remains in an excellent state of preservation (fig. 7) (Dunkerton, 1986).

Although, as mentioned above, ultramarine, of both natural and artificial varieties, is stable to ammonia and caustic alkalis in ordinary conditions, it has been reported that cases have occurred of artificial ultramarines fading when in contact with lime, when, for instance, it is used to color concrete or plaster (see Ultramarine, Artificial). These findings lead to speculation that possible fading of the natural pigment may possibly be the result of its contact with the lime plaster of fresco paintings.

Microchemical Tests

Heat Resistance

This distinguishes ultramarine from azurite or Prussian blue. The sample of pigment or the untreated paint fragment is placed on a platinum spoon, wire, or foil or in a hard-glass combustion tube, and is heated to redness. On cooling, the heated sample may be observed under the microscope or with a hand-lens. The blue color of ultramarine remains unchanged, whereas azurite is converted to black copper oxide, and Prussian blue is converted to orange—brown ferric oxide, while indigo sublimes with a blue vapor leaving no appreciable residue. Smalt, cobalt blues, manganese blue, and phthalocyanine blues are also heat-resistant in these conditions, but may be distinguished from ultramarine by their lack of reac-



Fig. 7 Thin cross section from the Virgin's blue robe in Sassoferrato's *The Virgin in Prayer*. National Gallery, London, No. 200. The ultramarine glaze is of a striking color and purity. Transmitted light, 738x. Photo: A. Roy.

tion with acids. For discussion of this topic, see articles by Bernstein (1945), Gettens and Stout (1935–1936), and Augusti (1935).

Test for Hydrogen Sulfide Liberated by Acid

A drop of dilute HCl-3M, or approximately 1 part concentrated HCl to 3 parts water by volume-placed on the sample of pigment or the fragment of paint containing ultramarine usually rapidly destroys the blue color and liberates hydrogen sulfide. Bubbles of gas can generally be seen arising from the blue particles, although these may not be evident if the particles are locked up in an oil- or oil-resin medium; however, since bubbles of carbon dioxide may also be evolved, either from calcite present as an impurity in the natural mineral, from the blue copper carbonate pigment, azurite, or from white lead present in the paint sample, it is advisable to test for sulfide. In sizeable yet still quite small samples—that is, greater than about 1 mm diameter—it is often possible to detect the characteristic smell of "rotten eggs" associated with H₂S. Where this fails, chemical tests must be applied. As suggested by De Wild (1929), place the sample in the hollow of a cup slide, add a drop of dilute hydrochloric acid, and cover at once with a glass cover slip on the underside of which has been pressed a small slip of filter paper moistened with lead acetate solution. Any hydrogen sulfide evolved will produce a brownish black stain of lead sulfide on the paper.

This author has found that the test can be speeded up and simplified by placing the sample directly on a piece of commercially prepared lead acetate test paper and treating it with a drop of dilute HCl. The blue color of the pigment disappears, being replaced by a brownish black stain of lead sulfide around and beneath the sample. In the case of very small samples, the test may be carried out under the microscope.

Another method of detection was suggested by Bontinck (1939). This is to place the sample on a small square of bright silver foil then add a drop of dilute acid as before. Silver sulfide gradually forms, beginning as a yellowish stain and developing through brown to black. It is better seen with the naked eye or a low-power lens than under the microscope. The silver foil may be polished clean with moist chalk before reuse. Again, this author has found that the same principle can be applied more simply, in this case by placing the sample on a piece of spot-test paper freshly impregnated with silver nitrate solution and dried. A black stain of silver sulfide forms when the ultramarine is treated with dilute acid.

If the sample is rather small or if there is some doubt as to whether the test for sulfide is positive, a blank test should be run simultaneously, using the reagents only (dilute acid, test papers, or silver foil) and comparing the results with those of the test carried out on the pigment sample. In the case of a sample in which the pigment is locked up in a good deal of oil- or oil-resin medium, a preliminary treatment with a drop of concentrated ammonia solution will disintegrate the medium sufficiently for the pigment to react and is without any effect on ultramarine. Gently warming will evaporate off any excess ammonia and leave the sample ready for testing for sulfide in any ultramarine present. No figures for the sensitivity of this test are quoted in the literature.

Effect of Sodium Hydroxide

The pigment sample or paint fragment is treated with one or two drops of dilute (2M, that is, 80 g dissolved in water and diluted to one liter) sodium hydroxide, on a microscope slide, a platinum spoon, or in a hard-glass microcombustion tube according to size. The treated sample is then warmed gently for about a minute. In these conditions ultramarine is unaffected, azurite particles are attacked, and the copper present converted into pale blue copper hydroxide, which on heating converts to black copper oxide, while Prussian blue loses its blue color and leaves an orange—

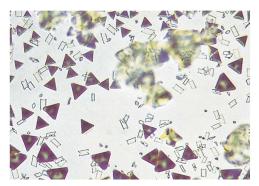


Fig. 8 Tetrahedral crystals of sodium uranyl acetate formed in testing for sodium in synthetic ultramarine with uranyl acetate. The colorless crystals are recrystallized reagent. Transmitted light, 400x.

brown residue of ferric hydroxide. When the residue from the treatment is examined under the microscope or through a lens, it is as well to add a drop of water to dissolve any white residue of sodium carbonate, which may have been formed during heating the hydroxide, so that any blue particles are not obscured.

Test for Sodium with Uranyl Acetate UO₂(CH₃COO)₂.2H₂O to Form Na(CH₃COO)₂.UO₂(CH₃COO)₂

The pigment sample is dissolved, or the paint fragment treated, with a drop of moderately concentrated (6M, or approximately 1 part glacial acetic acid to 3 parts water by volume) acetic acid. A drop of the uranyl acetate reagent (a concentrated aqueous solution acidified with acetic acid) is then added to the test drop. In the presence of sodium the reaction product is a salt of high molecular weight, strong crystallizing power, and low solubility in cold water, stable enough to crystallize out from hot water. It crystallizes out as very faintly yellow regular tetrahedra or triangular plates whose form is easily visible even at as low a magnification as 60x. Excess reagent separates as short, stout orthorhombic prisms. By transmitted light the perfect tetrahedra of the double acetate sometimes appears black because of total internal reflection (see fig. 8). Chamot and Mason (1932) suggested modified procedures in cases where there may be interference from other elements and discussed the effects of interfering elements on the test and means of counteracting them. It should be noted that the reagent is so sensitive to sodium that it should not be kept in ordinary glass containers, since there is a risk that it may take up sodium from the glass. Polyethylene containers or wax-coated glass are more suitable. Even uranyl acetate of analytical reagent quality contains a trace of sodium, so for this test it is important to carry out a blank test using only the reagents, and compare the result with that obtained from the paint sample.

Flame Test for Sodium

A platinum wire is cleaned by dipping it into concentrated hydrochloric acid then heating it in the hottest part of the Bunsen burner flame. It is clean when it imparts no color to the flame. The wire is dipped into a small amount of fresh concentrated hydrochloric acid in a watch glass, then the moistened wire is used to take up a little of the pigment sample or fragment of paint being tested. The wire is again heated in the nonluminous part of the Bunsen flame. If sodium is present in the sample, it will give an intense and persistent golden yellow color to the flame. Care must be taken to ascertain by means of a blank test with a cleaned wire that the sodium color is in fact derived from the sample and not from sodium salts contaminating the reagents or apparatus. If copper is present in the sample (from azurite, for example), and in sufficient quantity, it may impart a blue-green color to the flame. A flame test is unlikely to be applicable or useful except where there is sufficient sample left over for it after completing the other tests mentioned above.

All the above tests, with the exception of the flame test for sodium, can, with the aid of the microscope, be carried out successfully on a fragment of paint of no greater than 0.5-1.0 mm diameter.

All the above tests are equally applicable to artificial ultramarine which will give results identical to those given by the natural product. Simple chemical tests cannot distinguish the two, and optical examination (see above) or x-ray diffraction must be used for this purpose.

Criteria for Certain Identification

Natural ultramarine can usually be recognized microscopically with little difficulty. The principal particle and optical characteristics are: blue color by transmitted and reflected light; flattish particles of irregular size and shape having fractured edges; low refractive index of the blue particles; presence of colorless crystalline impurities; and absence of

birefringence of the blue particles but presence of highly birefringent calcite crystals among the colorless crystalline impurities. The chief chemical characteristics are: unaffected by heating up to redness; unaffected by ammonia or caustic alkalis under test conditions described; blue color destroyed by treatment with dilute acids with hydrogen sulfide being evolved; and the presence of so-

Microscopical identification may be confirmed by carrying out one or two of the chemical tests listed. The same sample (already examined microscopically) may serve for several tests-for example, a pigment sample or paint fragment tested for effect of heating may be further tested with acid or alkali.

Instrumental methods for identifying both natural and artificial ultramarine are listed below.

Emission Spectrometric Analysis

Identification of ultramarine by this method seems to have not been regularly used, although it could ascertain the presence of sodium (Na), silicon (Si), aluminum (Al), and also, with modified apparatus and conditions, sulfur (S). Emission lines for silicon and aluminium are readily detected in the ultraviolet part of the spectrum, but are, of course, also produced in the spectra of earth colors and other material likely to be found in paint samples. A specific instance of the use of the laser microprobe to show by spectrographic analysis the content of natural ultramarine in a paint cross section was reported by Bomford et al. (1980).

Hermann Kühn (private communication) reported that at the Doerner Institute in Munich spectrometric analysis of pigments by this means is routinely carried out and included detection of the elements mentioned above.

X-ray Diffraction Analysis

X-ray powder photographs of both natural and artificial ultramarine, in connection with identification of the pigments in paintings, were published by Young (1959) and Froentjes (1962). X-ray diffraction is not only an excellent method for detecting the presence of ultramarine but also serves to give detailed information of mineral impurities present in the natural pigment (see fig. 9 and table 1).

Table 1 X-ray Diffraction Data for Ultramarine^a *Lazurite*

Synthe Ultran JCPD 2-032	marine S	Ultran	hetic narine · F80°	Sar-i- Afgha JCI 17–1	Sang, nistan	Lazı (Mik Table	heev	Bade	zurite akshan er F82 ^f	Paint S Kariye Freer I	Çamii	Paint S Bām Fro F14	iyān eer
d(Å)	I	d(Å)	I	$d(\mathring{A})$	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
_		_		_		10	100	10.41 10.08	18 18	10.38 7.64	17 27	 10.07 7.64	13 64
6.49	80	6.46	60	6.43	40	6.4 5.1	20 20†	6.51 5.14	40 21†	6.24	39	6.42	17
4.59	10	4.55	42	4.86 4.54	6 18	4.5	50	 4.57	26	4.91	62	4.82 4.57	34 57
_		4.11	22	=		4.08	50	4.07 —	17	4.28 4.06 3.91	88** 73 87†	4.29 4.06 —	96** 66
3.74	100	3.72	100	3.71	100	3.74	100	3.73 3.65	100 29+	3.71	100	3.82 3.71 3.62	69 100 + 61
_		_ 	20	3.56	6	_		3.53 3.45	18† 16			3.50	39†
_		3.41	20	3.43 — 3.21	6 16	3.35 3.20	70** 60+	3.41 — 3.20	19 12+	3.36 3.20	45** 45+	3.35 3.22	49** 31 +
_		_		3.03	6	2.99	100+	3.04	39*	3.05 2.96	84* 45+	3.19 3.07 2.97	36 72* 21 +
2.91	100	2.88	58	2.872	45	_		2.90	42	2.88	53	2.88 2.80	42 13
_		_		2.755	4	2.78 2.75	6+† 4	2.78 — —	67+†	 2.70	28	2.69	21
2.65	100	2.63	73	2.622	80	2.64	70	2.64 2.58	69 12+	2.62	28	2.62	39
	10	2.49	11	2.502	4	2.53	90+†	2.51	17+†	2.50	25+	2.50	16+
2.45	10	2.43	13	2.427 —	16	2.43	50	2.45 2.39	27 7+	 2.36	25	2.44 	17
_		_		_		_		 2.33	6	2.35	14	_	
2.29 — 2.16	40 60	2.28 — 2.15	28 38	2.272 2.233 2.194	25 4 4	2.30 2.21 2.14	50 50 + 50	2.29 2.21 2.16	30 10+ 50	2.29 2.23 2.14	31 39 + 45	2.28 2.22 2.14	21 29 + 34
	10	2.04	11	2.141 2.087	35 4	2.02	70†	2.10 2.03	19* + 12†	2.13 — 2.03 1.96	48**+ 27† 34	2.09 2.00	31* 13
1.95 — —	10	1.94 —	10	1.937 — —	4	1.94 — —	20	1.95 1.91 —	8 8*	1.91 1.91	56* 56 db	1.90	19
_		_		_		 1.86	50+†	1.88 — 1.84	11* 7+	 1.84	34+	1.87	21*†
Ξ		_		_		_		1.80	29	_		1.82	25+
1.79	80	1.79 — 1.76	44 13	1.782	30	1.78 — —	50	_		1.79 1.78 —	37 22+	1.78	34+
_		- - -	13	1.734 1.702	2 2	1.74	50+†	1.70	10	1.74 1.70	20 + 8	1.74	9+†
1.66	20	1.66	12	1.660 1.635	6 2	1.68	70**+	1.67 — —	8**+	1.66 —	15**;	1.68 1.67 1.65	4+ 13**+ 9**
1.62	60	1.61	22	1.606	20	1.62	70	1.62	25	1.62 —	28	1.62 1.61	21 17* +
1.57	40	1.56	15	1.559	10	_		1.59 1.57	10+ 14+	1.56	22+	1.57 1.56	5 + 4
1.52	40	1.52	16	1.514	10	1.545 1.517	90** + 50	1.54 1.53	8** 14	1.52	28	1.54 1.52	9 15

Table 1 Continued

2-0325 ^b Freer F80 ^c 17-749 ^d Table 689 ^e) Freer F82 ^f Freer F1445 ^g		144 ^h
$\overline{d(\mathring{\text{A}})}$ \overline{I} $\overline{d(\mathring{\text{A}})}$ \overline{I} $\overline{d(\mathring{\text{A}})}$ \overline{I} $\overline{d(\mathring{\text{A}})}$ \overline{I} $\overline{d(\mathring{\text{A}})}$ \overline{I}	d(Å)	I
	_	
1.48 40 1.48 9 1.475 14 1.480 20† — 1.48 21†	1.48	13†
1.44 7**+ 1.44 22**+	1.44	8**+
	_	
	1.41	4+
1.40 6+ _	1.40	5
	1.37	21
1.36 5*† _	_	
	1.34	13
	1.31	12 + †
1.29 40 1.29 14 1.286 6 1.291 20 1.29 7 1.28 17	1.28	5
1.267 2 1.275 20		
	1.24	17
1.225	1.21	8
<u> </u>	1.15	16
1.14 5**	1.14	13**
	1.09	10**
1.06 14 1.042 6 — 1.05 8+ 1.06 21+	_	
1.04 12 1.04 18 +	-	
1.016 4 — 1.02 4 —		
927 288	.87	10
873 286	.85	6
	_	

a. Compiled by W. Thomas Chase, III.

- * Probably caused by presence of calcite in sample.
- ** Probably caused by presence of quartz in sample.
- + Probably caused by presence of diopside in sample.
- † Probably caused by presence of forsterite in sample.

b. Ultramarine blue, JCPDS File 2-0325. (Courtesy of JCPDS International Centre for Diffraction Data.) Taken from E. Gruner, Z. Anorg. Chem. 224, 360 (1935). Conditions: CuK α radiation with filter, I/I_1 visual; $a_0 = 9.18 \text{ Å}$.

c. Synthetic ultramarine, Schmincke. Freer film F80. Conditions: CuKα radiation, Ni filter, I/I, densitometer. No back reflection seen; measurements not corrected for film shrinkage. Some impurities, especially quartz, can be observed microscopically in this synthetic ultramarine. Silica is probably present in all ultramarine samples both natural and synthetic.

d. Lazurite from Sar-i-Sang, Afghanistan, JCPDS File 17-749. (Courtesy of JCPDS International Centre for Diffraction Data.) Department of Geology and Mineralogy, University Museum, Oxford, England. Conditions: CuKα radiation, Ni filter, I/I₁ calibrated strip; $a_0 = 9.09 \text{ Å}$.

e. Lazurite from Afghanistan. Table 689 (p. 659) in V. I. Mikheev, Rentgenometricheskii Opredelitel Mineralov (Moscow, 1957), vol. I. Source of data: XRDC II (1964). First supplementary cards of x-ray diffraction data, compiled and published by joint committee of ASTM, American Society for X-ray and Electron Diffraction, and Institute of Physics of London. Conditions: Cu radiation, Al filter. See Mikheev's table at top of page 658 for a list of lattice constants (a_o) of ultramarines.

f. Lazurite from single crystal, Badakshan. Department of Mineral Sciences, Smithsonian Institution, specimen C5231. Freer film F82. Conditions: CuKα radiation, Ni filter, I/I₁ densitometer. Corrected for film shrinkage.

g. Blue paint from Kariye Çamii, Istanbul; blue robe of angle in dome of Chora. Freer film F1445. Conditions: CuKα radiation, Ni filter, I/I_1 densitometer. Back reflection not visible; measurements not corrected for film shrinkage.

h. Blue paint from a fresco at Bāmiyān, Afghanistan. Freer film F1444. Conditions: CuKα radiation, Ni filter, I/I₁ densitometer; measurements corrected for film shrinkage.

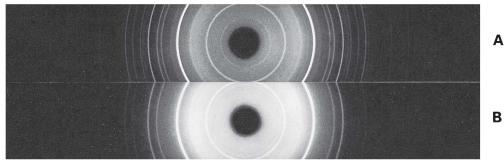


Fig. 9 X-ray powder diffraction patterns for ultramarine.

A. Lazurite from a single crystal. Badakshan, Kokcha District, Afghanistan. Department of Mineral Sciences, Smithsonian Institution, specimen C5231. Calcite line marked.

B. Ultramarine. Commercial dry pigment. Hatfields' Color Shop, 1940.

Photographs not to be used for measurement purposes. XRD patterns by Elisabeth West FitzHugh.

X-ray Spectrometry (X-ray Fluorescence) Analysis

The characteristic elements of ultramarine may be detected in principle by x-ray fluorescence analysis on the surface of an object, although it would only rarely be the most appropriate means of identification. Modern x-ray spectrometry is increasingly capable of determining the presence of the lighter elements, and the detection of sodium, aluminum, and silicon in conjunction with sulfur in blue paint would strongly suggest the use of either natural or synthetic ultramarine. The energies of the relevant identification lines for energydispersive macroanalysis were given by Hanson (1973). Greater sensitivity and separation of peaks, particularly for elements of relatively low atomic number, may be achieved using wavelength-dispersive systems. The elements detected can, of course, arise from any component of the paint, and where a layer structure is present, penetration of the x-ray beam and excitation of constituents of the underlayers may serve to confuse the results of identification. Since ultramarine is frequently used in mixture with lead white, the interference of fluorescence lines for lead and sulfur may lead to one or other elements being missed (Goldstein et al., 1981).

The distribution of ultramarine may be "mapped" in paint cross sections and similar samples using energy-dispersive x-ray microanalysis (EDX) in the scanning electron microscope. An example of the use of this method was given by Vendl et al. (1984) for samples from a painting by Raphael. Element distribution maps for alumi-

num and silicon show clearly the location of a layer containing natural ultramarine.

In general, x-ray fluorescence (XRF) is not the most suitable method for the identification of ultramarine and perhaps would only be used in studies where a detached sample is entirely ruled out, or where the pigment is suspected to have been used unmixed with any other in a single layer, for example, in works on paper. Positive identification is probably best achieved by other means, particularly optical and chemical microscopy, x-ray diffraction analysis, or Raman spectroscopy (see below), each of which may be successfully performed on single pigment particles or minute samples.

Visible, Infrared, Raman, and Ultraviolet Spectrophotometry

A color reflectance curve of natural ultramarine painted on rag paper with thin parchment-glue medium was published by Barnes (1938–1939) who showed the dominant wavelength to be 474.4 nm, relative brightness to be 18.64%, and the excitation purity to be 49.2%.

Spectral reflectance curves in the visible range for both natural and artificial ultramarine in acrylic medium are shown in figure 10 with the appropriate chromaticity data.

Staniforth (1955) reports, not surprisingly, that retouching matches for natural ultramarine are best achieved using the synthetic pigment.

Infrared spectra of natural ultramarine (lazurite) were published by Milkey (1960) and Moenke (1962); they show strong complex broad absorp-

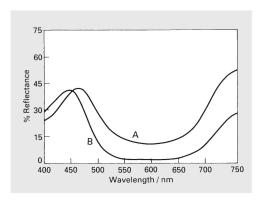


Fig. 10 Spectral reflectance curves for (A) natural ultramarine and (B) synthetic ultramarine in acrylic medium, 400-760 nm. CIE data: natural ultramarine (L* = 46.61, a* = 6.302, b* = -35.65); synthetic ultramarine (L* = 25.25, a* = 44.96, b* = -69.14). Courtesy of D. Saunders.

tion maxima at 1110–1088 cm⁻¹ and 1016–1010 cm⁻¹ arising from stretching modes in the tetrahedral silicon–oxygen (Si–O) units that make up the skeleton of the mineral. The spectrum is closely similar to those of the other minerals of the felspathoid sodalite subgroup to which lazurite belongs.

Guineau (1984), using the laser Raman microprobe, was able to show the presence of lazurite on a twelfth-century French missal by locating a strong Raman absorption at 548 cm^{-1} which is attributed to the S_3^- ion. The technique may be used nondestructively on small delicate objects.

The infrared reflectance of ultramarine is comparatively high, as shown by Farnsworth (1938–1939) and this property is sometimes useful for distinguishing it from several of the other earlier-known blue pigments such as azurite, indigo, and Prussian blue—all of which have low infrared reflectance. Figure 11B shows an infrared photograph of a detail (fig. 11A) of the *Virgin and Child* by Duccio (National Gallery, London, no. 566) in which the Virgin's deep blue ultramarine cloak shows as a light area. For comparison in figure 12B, the deep blue azurite robe of the Virgin in a *Virgin and Child* by Dieric Bouts (fig. 12A) (National Gallery, London, no. 774) appears quite dark in the infrared photograph.

Important work has been carried out by Elskens (1960) at the Institute Royal du Patrimoine Artis-

tique in Brussels, on the application of spectrophotometry in the visible and near ultraviolet wave band to thin cross sections of paintings, as prepared by Jean Thissen of the same laboratory. The first study by this method was made on a thin section of blue paint from the mantle of the Virgin in the Van Eyck polyptych, *The Adoration of the Mystic Lamb*. Natural ultramarine, of which spectrophotometric curves are reproduced, was one of the pigments identified in the cross section.

X-radiography

Ultramarine, since it contains no elements of high atomic number, is comparatively transparent to x-rays and, unless mixed with a pigment of high x-ray absorption such as white lead, it will appear only as a dark area on x-radiographs of paintings. De Wild (1929) gave the mass absorption coefficient for a wavelength of 0.708 Å as 4.0, as compared with values of 81.7 for lead white (see chapter 3) and 26.0 for azurite (see chapter 1) using the same wavelength.

Terminal Date

Although the use of natural ultramarine must have suffered a sharp decline with the introduction of the synthetic form in 1828 (see Ultramarine, Artificial), some artists appeared to have held it in high esteem. As noted above, Schmidt (1847) gave detailed instructions for the extraction of the pigment from the mineral, while at the same time describing the production of the synthetic form. He remarked that genuine ultramarine is always exceedingly costly, 80–100 or even as much as 200 francs an ounce, while synthetic ultramarine was being sold in Paris for 25 francs an ounce.

An enquiry made by the author in the 1960s to the principal English color merchants produced some interesting statistics. Reeves & Sons Ltd. ceased to supply natural ultramarine as a watercolor and oilcolor in 1900 and 1912, respectively. Rowney's Ltd. offered genuine ultramarine in their catalogue of 1864 at a price of £8 per ounce, and the pigment continued to appear until 1896 when the price was £7 17s. 6d. per ounce, but it is then absent from catalogues from 1907 on. The same company first listed ultramarine ash in their 1892 catalogue and it continued to be available until 1916, disappearing again from the 1920 list (A. R. French, technical director, Rowney-Daler Ltd., private communication). Roberson & Co. mentioned that in the early part of this century



Fig. 11 Detail of the Virgin and Child from a triptych by Duccio. National Gallery, London, No. 566. A. Panchromatic photograph. The Virgin's deep blue cloak is painted in natural ultramarine.



B. Infrared photograph. The Virgin's deep blue cloak appears light because of the high reflectance of ultramarine for infrared light.



Fig. 12 Detail from the *Virgin and Child with Saints* by Dieric Bouts. National Gallery, London, No. 774.

A. Panachromatic photograph. The Virgin's deep blue bodice is painted in azurite and the light red cloak in vermilion.



B. Infrared photograph. The Virgin's deep blue bodice appears dark because of the low infrared reflectance of azurite, and the red cloak appears lighter because of the high infrared reflectance of vermilion.

their firm purchased supplies from Italian suppliers who brought it in small batches to London via Paris and probably prepared it in their own homes by the traditional method. Winsor & Newton Ltd. always seem to have made a speciality of stocking the natural pigment ever since the establishment of the firm in 1832, although in that same year they were simultaneously offering the artificial pigment. Since 1940 they have had difficulty in maintaining a supply, but apparently a certain demand still exists and both natural ultramarine and ultramarine ash continued to be offered in the 1980s when batches of lapis lazuli from Afghanistan allowed it to be made (P. J. Staples, technical director, Winsor & Newton Ltd., private communication). The entry in Winsor & Newton's catalogue for 1955 would, however, have limited the use of the natural pigment to the richest painter or the most determined forger:

Ultramarine Genuine no. 1 120s. 0d. per ounce Ultramarine Deep (synthetic) 1s. 6d. per ounce

The cost of the natural pigment was then eighty times that of the synthetic. It should be pointed out, however, that Van Meegeren (see Notable Occurrences) went to the expense and trouble of using natural ultramarine in some of his forgeries of paintings by Vermeer and De Hoogh (although, unknown to him, it had been adulterated with cobalt blue).

Notable Occurrences

- (a) On wall paintings of the sixth to seventh century A.D. in the cave temples at Bāmiyān in Afghanistan, described by Gettens (1937–1938a). Gettens (1937–1938b) also identified ultramarine in wall paintings in Chinese Turkestan of the fifth to eighth centuries A.D.
- (b) On two Chinese paintings on silk said to have come from Dun-huang in Western Kansu Province of China:
 - (1) Freer Collection no. 30.36. Painting dated A.D. 968 Avalokiteśvara with Attendant Divinities. Sample of blue from halo.
 - (2) Freer Collection no. 35.11. Painting dated tenth to eleventh centuries *Ksitigasbba and Attendants in a Landscape*. Sample of blue from the robe of the central figure. (Rutherford J. Gettens, private communication.)
- (c) In the wall paintings of the Brihadisvara Temple at Tanjore (eleventh to twelfth century

- A.D.). An investigation into the materials and method was made by Paramasivan (1937–1938). At this site, ultramarine seems to have been the most readily available blue pigment and was used mixed with yellow ochre to give green, a practice not encountered in Europe.
- (d) On a Romanesque fresco of the twelfth century A.D. in the German Romanesque church of Idensen. Described by Geilmann (1938).
- (e) On an Armenian illuminated manuscript *The Four Gospels* (c.twelfth century) f. 183 recto; Freer Gallery of Art no. 50.3. Identification made by Rutherford J. Gettens, see figure 5A and B.
- (f) In wall paintings of the fourteenth century A.D. in the Byzantine church of Our Saviour, Monastery of the Chora (Kariye Çamii), Istanbul. Identified by Gettens and Stout (1958), as the brighter and purer blue of blue draperies otherwise painted in azurite.
- (g) On the drapery of a Romanesque polychromed limestone figure of Moses, St. Mary's Abbey, York, England, dated c.1180. Identified by Ashok Roy.
- (h) Plahter (1984) reported the use of natural ultramarine in oil on a polychromed wooden crucifix dated about 1170/1190 from Hemse Church on Gotland. She also noted the pigment on a fragment from an early Norwegian oil painting on panel (Historisk Museum, Bergen), c.1260/1280, as a pale gray—blue layer for the draperies of figures, possibly simply ground lapis lazuli or "ultramarine ash" (Plahter & Plahter, 1976).
- (i) On a French painted ivory c.1300 in the collection of the Victoria and Albert Museum, London (*The Soissons Diptych*, no. 211–1865). It is not known if in works of this kind whether the carving and painting are contemporary. Identified by Ashok Roy.
- (j) With lead white in oil-medium on a fragment of wall painting of the mid-fourteenth century from St. Stephen's Chapel, Westminster (now in the British Museum, London). The surface of a sample had a glaze of pure ultramarine (Van Geersdaele & Goldsworthy, 1978). Identified by the author.
- (k) The pigment was present on a rudimentary artist's palette discovered on the spandrel of a fourteenth-century Italian panel painting, *The Virgin and Child*, by Paolo Veneziano in the collection of the Louvre, Paris. Reported by Bazin et al., (1958).

- (1) In numerous locations on the Duccio polyptych, the *Maestà* in Siena, a work completed in 1311. Reported by Mora and Torraca (1959). It is interesting to note that, on three of the predella panels from the same altarpiece now in the National Gallery, London (*The Annunciation*, no. 1139; *Jesus Opens the Eyes of a Man Born Blind*, no. 1140, and *The Transfiguration*, no. 1330), natural ultramarine was identified as the blue of the robes of Christ and the Virgin (Bomford et al., 1989).
- (m) In Dieric Bouts' retable of the *Holy Sacrament* at Louvain and in the Van Eyck polyptych, *The Adoration of the Mystic Lamb*, Church of St. Bavon, Ghent (Coremans, 1954).
- (n) As a component in purple colors of costumes in Botticelli's early panel painting, *The Adoration* (National Gallery, London, no. 592). The purple color is produced by a glaze of coarse ultramarine particles thinly scattered over an opaque underpaint of white lead tinted pink with a madder-type red lake pigment. The materials and technique are described by Ruhemann (1955).
- (o) As very high-quality pigment in the bright blue draperies of the Virgin in Sassoferrato's *The Virgin in Prayer* and *The Virgin and Child Embracing* (National Gallery, London, nos. 200 and 740, respectively) (Dunkerton, 1986).
- (p) Specific instances reported in a number of Early Netherlandish, Flemish, and Dutch easel paintings dating from 1437–1810 and examined by De Wild (1929).
- (q) As a component of purple paint of drapery in Bronzino's *Allegory* (National Gallery, London, no. 651), mid-sixteenth-century Italian school. In this case, the purple color was obtained by a physical mixture of white lead, ultramarine, and a crimson-colored lake pigment. Ultramarine is also the principal blue pigment to be seen in this picture. Recorded in the National Gallery's archives (London).
- (r) In six pictures by Titian in the National Gallery, London (nos. 4, 270, 635, 1944, 3948, and 5385), dating from the very early *Holy Family*, no. 4, to the *Madonna and Child*, no. 3948, which must have been painted not long before Titian's death in 1576. Details of identification recorded in the National Gallery's archives (London).
- (s) In a number of paintings by Poussin in the collection of the Louvre, Paris. Reported by Delbourgo and Petit (1960).

- (t) As the blue pigment of the sky and saddlecloth in Van Dyck's *Portrait of Charles I on Horseback* (National Gallery, London, no. 1172), underpainted in these areas with smalt. Identified by the author (1956).
- (u) As a glaze and tint for the blue drapery in Van Dyck's *Charity* (National Gallery, London, no. 6494), underpainted with indigo. Identified by Ashok Roy.
- (v) In numerous samples from Rubens' altarpiece, *The Descent from the Cross*, in the Cathedral of Antwerp. Coremans and Thissen (1962) reported that natural ultramarine, as well as being used for glaze, is, in this picture (for example in certain of the draperies) sometimes mixed with pigments other than white lead, such as indigo.
- (w) Mixed with lead white for the sky of Rubens' *The Watering Place* (National Gallery, London, no. 2924). Identified by Ashok Roy.
- (x) In a small area of the most intense blue of Cupid's sash in the Velázquez *Toilet of Venus* (the "*Rokeby Venus*") (National Gallery, London, no. 2057). The remainder of the blue sash is painted in azurite, while both the blue–gray draperies and the cool shadows of the flesh have smalt as the blue pigment. Recorded in the archives of the National Gallery, London.
- (y) In the blue paint of Rebecca's bodice, mixed with lead white, in Giovanni Pellegrini's *Rebecca at the Well* (National Gallery, London, no. 6332). Probably painted in England, early eighteenth century. Identified by Ashok Roy.
- (z) As highlights and glazes on the coat of the Viscount in William Hogarth's *The Marriage Contract* (National Gallery, London no. 113), one of the series *Marriage à la mode*, c.early 1740s (Bomford & Roy, 1982).
- (aa) In forgeries of Vermeer and De Hoogh [or De Hooch] painted by Van Meegeren in the present century. Although Van Meegeren went to the trouble and expense of procuring authentic lapis lazuli ultramarine, unknown to him, it had at some stage been adulterated with cobalt blue (a pigment of early nineteenth-century introduction). This fact was discovered during a subsequent scientific examination of the forgeries. A detailed account has been given by Coremans (1949).

Ultramarine Blue, Artificial

Synonyms

French ultramarine, French blue, Guimet's blue, New blue, Permanent blue, synthetic ultramarine.

Composition

Similar to that of natural ultramarine, approximately Na₆₋₁₀Al₆Si₆O₂₄S₂₋₄, but capable of considerable variation according to the ratio of the starting materials used in the manufacture and the conditions of preparation.

Date and Circumstances of Discovery

Artificial ultramarine is a pigment of comparatively modern invention. The first recorded observation of the substance seems to have been made by Goethe (Auden & Mayer, 1962), when in 1787, in the course of his Italian travels, he noticed blue deposits on the walls of lime kilns near Palermo. He remarked that the glassy blue masses were cut and used locally as a substitute for lapis lazuli in decorative work, although he did not mention whether or not the idea had arisen of grinding the material for use as a pigment. Among those who, some years later, observed similar phenomena was Tassaert, who found blue masses in soda kilns of the glass factory at Saint Gobin in France and, in 1814, submitted samples for analysis to the distinguished chemist Vauquelin (1824). Analysis showed that the blue material had a similar chemical composition to that of natural ultramarine derived from lapis lazuli. Tassaert communicated his findings to the Société

d'Encouragement pour l'Industrie Nationale with the suggestion that, on this basis, a method for synthesizing ultramarine might be investigated. In 1824 the Société offered a prize of 6,000 francs for the discovery of a workable industrial process whereby synthetic ultramarine could be manufactured at a cost of not more than 300 francs per kilogram (Société d'Encouragement pour l'Industrie Nationale, 1825). The prize was not awarded until four years later since earlier contestants had merely submitted imitations based on cobalt or Prussian blues and, as the Société reported, with no regard to the analyses of natural ultramarine that had been made by Désormes and Clément (1806) and subsequent workers. The prize was finally awarded on 4 February 1828 to Jean Baptiste Guimet who had set up a workshop in Paris; he evolved a successful process—an account of which he later published (Guimet, 1831)—for synthesizing ultramarine at the specified price, and had communicated his findings to the Société d'Encouragement in February 1828. Guimet's ultramarine sold for 400 francs per pound in Paris, the price of the natural pigment then being 3,000-5,000 francs per pound, according to quality. Independent of Guimet, C. G. Gmelin (1828), professor of chemistry at the University of Tübingen, discovered a slightly different method for making the pigment, based on the analytical results of Désormes and Clément, which he published only about a month later than Guimet's communication to the Société. Gmelin also applied for the Société's prize on the grounds that his discovery had been made before that of Guimet. The rival claims of the two were hotly

debated over several years; in France, at any rate, Guimet's right to the prize was upheld. Guimet started a factory for the commercial production of the pigment at Fleurieu-sur-Sâone in 1830, and meanwhile F. A. Köttig had begun making artificial ultramarine at the Meissen porcelain works. Very soon factories began to spring up all over France and Germany (Schmauderer, 1969) and some time later in England, Belgium, Austria, the United States, and elsewhere. Of the vast production, of course, only a small fraction would have been destined for use as artist's pigment.

Method of Manufacture

Since ultramarine is essentially a sodium aluminum sulfosilicate, the essential elements for its synthesis are sodium (Na), aluminum (Al), sulfur (S), and SiO₂, and the raw materials for manufacture generally comprise anhydrous sodium sulfate and/or carbonate, china clay, silica (in the form of quartz or sand), and sulfur. Coal, charcoal, or colophony supply carbon to provide a reducing atmosphere for the process. The purity of the ingredients is of considerable importance, one of the requirements being that they should be iron-free. The ingredients are finely ground, mixed, and heated in closed crucibles in a furnace at red heat for several hours in the absence of air. The product, after cooling, is a green mass known as green ultramarine or primary ultramarine. It is ground, washed free of soluble salts, and dried. To convert it to the blue form it is reheated at about 500°C. The final blue product is ground and washed free of soluble salts. The above process is known as the indirect process, since it involves two separate stages of heating. In the alternative direct process, the ingredients and their proportions and the time and condition of heating are arranged so that a single stage of heating gives the blue product. The hue, depth of color, and, to some extent, the chemical properties such as degree of vulnerability to acids, can be varied considerably by altering the proportions and type of starting materials and the conditions of manufacture. For example, ultramarines high in silica and low in sulfur, or vice versa, are prepared for particular requirements.

The depth of color of the resultant ultramarine is also partly governed by particle size. Those with large particle size have a deeper color, but finer particle size gives better tinting strength in mixtures with other pigments.

Although the main output of the industry is blue ultramarine, colors other than blue are made. Green ultramarine has already been mentioned as an intermediate stage in the indirect process, but it also has a limited application as a pigment. Violet and "red" (or, more correctly described, rather rosy violet) shades can be obtained by treating the blue pigment with sal ammoniac or dry hydrochloric acid gas at high temperatures, by which means some sodium is removed as sodium chloride. The resulting materials, if well washed, are as stable pigments as blue ultramarine but have rather poor tinting strength. They have some industrial use, but ultramarines other than blue seem not to have found a place in the artist's palette.

Good accounts of established manufacturing processes were given by Dippel (1849), Lichtenberger (1865), Zerr et al. (1908), Bock (1910), Rose (1910), Hoffmann (1902), and Kittel (1960). Numerous references to more modern modifications to the process than those above are to be found in the patent literature of almost every manufacturing country.

History of Use

Considering the high price of natural ultramarine, it seems likely that the synthetic product would have been rapidly adopted by artists soon after its invention. According to Mérimée (1828), the chemist and paint technologist who was a contemporary of Guimet, the latter supplied trial samples of his pigment to a number of artists almost immediately after he had succeeded in synthesizing it. Mérimée reported that Ingres used Guimet's artificial ultramarine for the drapery of one of the principal figures of his painting, The Apotheosis of Homer, on the ceiling of one of the rooms of the Musée Charles X in the Louvre. The painting is signed and dated 1827, which is the year before Guimet had communicated his findings to the Société d'Encouragement pour l'Industrie Nationale. The painting was removed from the ceiling in 1855 and replaced by a copy, but the original is in the Louvre collection of nineteenth-century French pictures. Laurie (1935) stated that artificial ultramarine was used by J.M.W. Turner. Considering Turner's dates (1775-1851) this would not be surprising, but the present author has so far been unable to find any evidence or original reference for Laurie's statement, and Hanson's (1954) report of analyses carried out on materials in Turner's painting boxes indicates the presence of cobalt blue and blue verditer but not ultramarine. either natural or artificial. The chemist Bachhoffner (1837) mentioned French ultramarine as having been discovered by Guimet and being available at the time as an artists' pigment. He added, "Fears are entertained for its permanency, but not more than all new pigments are subject to."

In the nineteenth century the manufacture of ultramarine was carried out principally in France and Germany. The London color merchants, Winsor & Newton, offered artificial ultramarine in their first catalogue of 1832 both in watercolor and as oilcolor in bladders. Over a long period this firm bought and offered the pigment as "Guimet's Ex. Fine Ultramarine," so it is likely to have been of French origin. Roberson & Co. introduced it about 1835 in both oil- and watercolor, and their records show that the demand for the synthetic pigment was immediate and that sales were considerable. Reeves & Sons Ltd. supplied the pigment in watercolor cakes by 1844, while Rowney & Co.'s records do not feature the synthetic pigment before 1850. Although catalogues of each of the color merchants mentioned above listed several shades of artificial ultramarine blue, none listed the green, red, or violet varieties, although these are still readily available as industrial pigments. Apart from the disadvantage of their rather low tinting strength, the lack of popularity of green, red, and violet ultramarines as artists' pigments may be because, whereas there is absolutely no substitute for the distinctive hue of blue ultramarine, there were available to the artist by the second half of the nineteenth century excellent pigments such as cobalt green, violets, and chromium oxide greens. It would be interesting to ascertain if ultramarines other than blue have played any role in the artist's palette.

Artificial ultramarine appears to have been a common component of the impressionist and post-impressionist palette; see Notable Occurrences and Delbourgo and Rioux (1974), Butler (1984), Roy (1985), Bomford and Roy (1983), and Bomford et al. (1990).

Chemical Composition

The problem of the structure of the ultramarine molecule and the origin of its astonishing color properties has by no means yet been fully solved, although the structure of the molecule corresponds approximately to that proposed by Leschewski and shown in figure 3. Reinhold Hoffmann summarized different types of compositions obtainable by varying the manufacturing process and the nature and proportions of the raw materials. The composition is very variable and is never

stoichiometric. For example, Reckitt's (Colours) Ltd. (1954) give the chemical compositions of their blue, green, and rose ultramarine as follows:

$$\begin{array}{lll} Blue & Na_{6.88}Al_{5.63}Si_{6.35}O_{24}S_{2.4} \\ Green & Na_{6.50}Al_{6.30}Si_{5.70}O_{24}S_{3.5} \\ Rose & Na_{5.88}Al_{5.76}Si_{6.21}O_{24}S_{2.52} \end{array}$$

Of the varieties other than blue, ultramarine green has been prepared containing chloride, and the reds and violets with ammonium and hydrogen (as hydroxonium) partially substituting for the sodium ion (Von Hofmann et al., 1969; Moser, 1972).

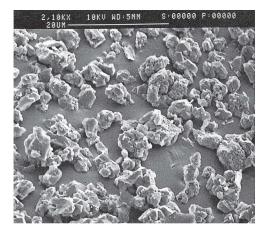
Particle Characteristics

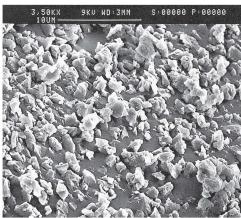
The artificial pigment has rounded particles of regular size and shape and is usually a finer particle size than the natural pigment. Reckitt's (Colours) Ltd. (1954) gave the range of particle size of their blue ultramarine, as produced from the ginding mills and before grading, as 0.5-5.0 μ in diameter (see fig. 13A-C). This author has, on occasion, noted particles of natural ultramarine of a diameter as much as 30 µ occurring in paint layers in cross sections of old paintings. Under the microscope, artificial ultramarine—in contrast to the natural—presents a more or less homogenous appearance, although at magnifications of above 150x upward fine colorless grains of silica can sometimes be seen. Blue granules of considerable size are sometimes seen in artificial ultramarine, but generally consist of aggregates of small particles, which can be detected at higher magnifications or if the pigment is well dispersed in a mounting medium such as glycerol or Canada balsam.

Figure 14 shows the small and comparatively uniform particle size in contrast to natural ultramarine (see also figs. 13A–C and 15).

Optical Properties

The blue particles appear rather more opaque by transmitted light than do those of the natural pigment, although the difference in refractive index of the two is not very significant. The refractive index—like that of the natural pigment—is comparatively low and is given by the Society of Dyers and Colourists and the American Association of Textile Chemists (1956) as 1.50–1.54 and by Reckitt's (Colours) Ltd. (1954) as 1.51. The blue particles, like those of the natural pigment, are isotropic and exhibit no optical activity, while op-





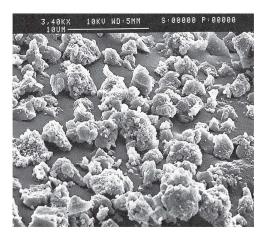


Fig. 13 Scanning electron micrographs of three grades of synthetic ultramarine manufactured by Reckitt's (Colours) Ltd. Gold-coated. Photos: A Roy.

- A. Sample H9957, printed at 1,344x.
- B. Sample H9960, printed at 2,240x.
- C. Sample H9964, printed at 2,176x.

tically active mineral impurities, notably calcite, are absent. Therefore, when viewed between crossed polaroids, synthetic ultramarine presents a completely dark field.

Chemical Properties

These appear to be closely similar to the chemical properties of natural ultramarine. As expected, considerably more modern scientific research has been done on the artificial pigment than on the natural pigment. As already observed, artificial ultramarine has a slight tendency to be more readily attacked by dilute acids than its natural counterpart. The so-called "acid-resistant" grades of ultramarine available in industry are not strictly so, but are ultramarines in which the particles are coated with silica (Feller, 1972) and are capable of withstanding mildly acid conditions for a few hours, one of their main uses being in the paper industry in processes where they are in contact with acid solutions of alum. Hoffmann (1876) stated that red and violet ultramarines when treated with acids are not so rapidly decolorized as blue ultramarine and do not evolve hydrogen sulfide. This difference was not apparent in the few samples of red and violet ultramarines tested by this author. Experiments by Leschewski and Podschus (1935) have shown that ultramarine is not attacked by caustic alkalis except by very prolonged and severe treatment such as prolonged boiling or fusion. Wilson (1935) reported, however, that the blue color of artificial ultramarine sometimes fades in the presence of excess calcium hydroxide, as when the pigment is used to color concrete or lime plaster. The reaction that takes place appears not to be an ion-exchange reaction (see below) of calcium (Ca) for sodium (Na) in the molecule, but a displacement of sulfur (Damle et al., 1942). A patent exists (Tanke, 1963) for the preparation of low-sulfur-content ultramarine for use in coloring cements.

Like other compounds of the class known as zeolites, ultramarine is capable of ion exchange. For example, by heating blue ultramarine in a closed tube with silver nitrate, Na⁺ ions are replaced by Ag⁺ giving so-called silver ultramarine, which is yellow in color. Similarly, polysulfide sulfur in the molecule may be replaced by selenium resulting in a crimson-red color. There might be a possibility of adapting some of these reactions for use as identification tests for the blue pigment. The subject of ion exchange in ultramarine has been fully treated by Barrer and Raitt (1954).

Permanence and Compatibility with Other Pigments

In ordinary conditions artificial ultramarine is comparatively permanent. Exposure tests have shown that it has good lightfastness (Rasquin, 1934). As mentioned, it is highly sensitive to acids and in urban atmosphere with a high concentration of sulfur dioxide or other acid fumes, posters printed with ultramarine blue and exposed outof-doors have been known to fade (Reckitt, 1954). An apparent case of "ultramarine sickness" (see Ultramarine, Natural) involving the synthetic pigment on a twentieth-century painting has been reported, but the loss of color in the paint film was in this case attributed mainly to loss of the paint medium rather than to degradation of the pigment (Bosshard, 1978). Experiments by Wagner and Mertz (1930) have shown that it is possible to mix ultramarine with white lead without chemical reaction occurring, provided that the white lead is reasonably free from lead acetate and that the paint medium is not unduly acidic.

General Pigment Properties

Artificial ultramarine pigment properties are similar to those of natural ultramarine. The Society of Dyers and Colourists (United Kingdom) and the American Association of Textile Chemists (1956) indicate that ease of grinding is good. The specified oil absorption given by the British Standards Institute (1952) is between 30 and 40. (This is the weight in grams of acid-refined linseed oil required to convert, by the rubbing method, 100 g of dry pigment to a coherent mass which will just not smear the glass plate on which it has been rubbed with a palette knife.) Properties of artificial ultramarine are fully described in papers by Havens (1948), Penot (1948), Tanke (1950), and Kumins (1954).

Microchemical Tests

All the microchemical tests proposed for natural ultramarine are equally applicable to the artificial pigment giving similar results. The natural and synthetic varieties of ultramarine cannot be distinguished with certainty by this means.

Criteria for Certain Identification

Chief diagnostic features are: characteristic pure blue color; rounded particles of regular shape and comparatively small and uniform size (disregarding aggregates); moderately low refractive index;

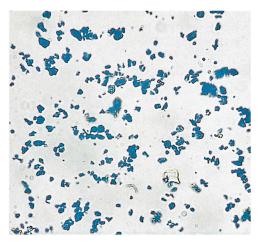


Fig. 14 Particles of synthetic ultramarine by transmitted light. Reckitt's (Colours) Ltd., No. H9957 (see also fig. 13A). Note the more rounded particle form than seen for the natural pigment. Mounted in Aroclor (n=1.66), 1,275x.

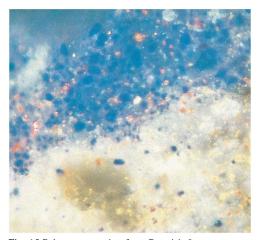


Fig. 15 Paint cross section from Renoir's *Les Parapluies*. National Gallery, London, No. 3268. Large amounts of synthetic ultramarine are used in the composition. The sample comes from the child's coat to the right edge of the picture. Reflected light, 893x. Photo: A. Roy.

blue particles not birefringent; and absence of any strongly birefringent colorless calcite crystals (a characteristic feature of the natural mineral) so that between crossed polaroids the field is dark. These particle and microscopical characteristics having been observed, the chemical constitution could be confirmed by applying one or two of the chemical tests described for natural ultramarine. Confirmation could be gained by x-ray diffraction

(see fig. 9) to ascertain that the mineral impurities generally associated with lapis lazuli were absent from the sample, but this is not an ideal method.

Emission Spectrometric Analysis

See Ultramarine, Natural.

X-ray Spectrometric (X-ray Fluorescence) Analysis

See Ultramarine, Natural.

Tuurnala et al. (1986) demonstrated that all the elements present in synthetic ultramarine may be detected by the new methods of particle-induced x-ray emission spectroscopy (PIXE) and particle-induced gamma ray emission spectroscopy (PIGME).

X-ray Diffraction Analysis

See Ultramarine, Natural (fig. 9 and table 1).

Visible, Infrared, and Ultraviolet Spectrophotometry

A color reflectance curve for wavelength between 400 and 700 nm for synthetic ultramarine, painted on rag paper with thin parchment-glue medium, was published by Barnes (1938-1939). He gave the dominant wavelength as 467.8 nm, relative brightness as 7.84%, and excitation purity as 75.1% (see also fig. 10). Mattiello (1946) published spectrophotometric curves using as a sample a compressed block of pure pigment unmixed with medium or inert, for wavelengths between 400 and 1,000 nm and by Reckitt's (Colours) Ltd. (1954) for wavelengths between 300 and 1,000 nm. The depth of color of the blue forms is related to the sodium content of the pigment (Moser, 1972). One of the most striking features of the curve is the rising reflectance in the red and the high reflectance in infrared—as also noted in the case of the natural pigment—for this reason, artificial ultramarine has been used in camouflage and heat-resisting paints.

X-radiography

See Ultramarine, Natural.

Notable Occurrences

Although it might be expected that artificial ultramarine would have been used in innumerable nineteenth- and twentieth-century paintings, and also featured in the detection of forgeries, records of specific identifications in the literature are very few. A possible reason is that fewer pictures of more recent date undergo the thorough technical and scientific examinations so frequently applied to "Old Masters." The following are some selected occurrences that have been reported:

- (a) Extensively in the second stage of painting (c.1886) of August Renoir's *Les Parapluies* (National Gallery, London, no. 3268). The first stage of the composition (c.1881) contains exclusively cobalt blue (Bomford et al., 1990). See figure 15.
- (b) Mixed with other pigments in Claude Monet's *Gare St. Lazare* (National Gallery, London, no. 6479) (Roy, 1985) and Édouard Manet's *The Waitress* (National Gallery, London, no. 3858) (Bomford & Roy, 1983). Also detected microscopically and with the electron micro-beam probe in a blue highlight on the water of Monet's *Waterlilies* in the National Gallery, London (no. 6343).
- (c) In paintings by Manet, Renoir, and Paul Cézanne in the collection of the Musée du Louvre, reported by Delbourgo and Rioux (1974), and in eight paintings by Cézanne, identified by Butler (1984). In Cézanne's *Mountains in Provence* (National Gallery, London, no. 4136) (Roy, 1985).
- (d) In the deepest blues and in certain samples of mixed green from Vincent van Gogh's *Cornfield with Cypresses* (National Gallery, London, no. 3861). Identified by Ashok Roy.
- (e) Reported by Kühn (1969) in a number of nineteenth-century German paintings in the Schack-Galerie, Munich, including works by Arnold Böcklin, Anselm Feuerbach, Franz von Lenbach, Carl Rottmann, and Ernst Willers.
- (f) Identified by Van Asperen de Boer (1975) on two carved wooden reliefs dated 1873 from Pannerden, Holland.
- (g) Used unmixed with any other pigment in a deep blue area of a collage and gouache painting, *L'Escargot*, by Henri Matisse (Tate Gallery, London, no. T540), dated 1953.
- (h) In a forgery claimed to be a painting by Frans Hals, *The Merry Cavalier*. The question of the authenticity of this painting was the subject of a lawsuit. An account of the matter was given by Veth (1925) and also by De Groot (1925) who, although he strongly disputed the scientific evidence, including the validity of the microscopic identification of synthetic ultramarine, reproduced most of the significant documentary evidence of the case in his book on the subject.

- (i) In two areas of overpaint on the Van Eyck polyptych, *Adoration of the Mystic Lamb*, on the Virgin's blue mantle in the panel depicting the Virgin reading (Coremans, 1954) and in the sky of the center panel (Jean Thissen, private communication).
- (j) In a restorer's mixture with other pigments to match embrowned "copper resinate" on the extended edges of Raphael's *St. John the Baptist Preaching* (National Gallery, London, no. 6480) (Braham & Wyld, 1984).
- (k) Identified on occasion by Rutherford J. Gettens (private communication) in pigment mixtures used in making artificial patina on Chinese bronzes.

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Lead White

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Current Terminology

English: lead white (sometimes white lead)

French: blanc de plomb German: Bleiweiss

Italian: bianco (biacca) di piombo

Spanish: plomo blanco

Obsolete Terminology and Synonyms

Flake white, Cremnitz white, Krems white, Vienna white, Berlin white, silver white, slate white, cerusa (or cerrussa), hydrocerussite (modern mineralogical name); other less common names are noted in Harley (1982).

Composition

The common lead white of commerce is the basic carbonate, 2PbCO₃.Pb(OH)₂ (CI Pigment White 1). Other varieties, Kalkow's lead white, and Falk's lead white are said to have been produced to a limited extent (Kühn, 1967) but have not been reported in paintings.

Normal lead carbonate, PbCO₃, corresponding to the mineral cerussite has rarely been used (see Notable Occurrences), although it often occurs as an impurity in the basic carbonate (see below). Stewart (1950) reported that a form

chloride, in two modifications, was regularly used in Japanese painting on silk and paper in the thirteenth and fourteenth centuries in addition to basic lead carbonate. Harley (1982) indicated that, according to Field's Practical Treatise of 1795, "white precipitate of lead," which was sulfate of lead, was used at one time in watercolor painting, and that it was still available in the 1830s, being sold in bottles under the name "Flemish white." In paintings, admixtures of lead white with other whites may be encountered. The ground layers of William Hogarth's series, Marriage à la mode (National Gallery, London, nos. 113-118) are of lead white combined with calcium carbonate (Bomford & Roy, 1982). Harley (1982) mentioned admixture of lead white with chalk for making opaque watercolor. Van de Graaf (1961) also mentioned that in the sixteenth and seventeenth centuries the Dutch painters used a priming

of lead white mixed with chalk, they called it *loot* wit (ceruse or Spanish white). This practice has been confirmed by chemical analytical studies car-

ried out in Brussels on Peter Paul Rubens' Descent

from the Cross. Here the imprimatura (priming) is

a mixture of chalk and lead white (Coremans &

Thissen, 1962). Other examples are the primings

of two pictures by Jan Vermeer in the National

Gallery, London: no. 1383, A Young Woman

of basic lead carbonate corresponding to 4PbCO₃.2Pb(OH)₂.2PbO has been manufactured

in this century. Other white-colored lead salts, the

sulfate, chloride, hydroxide, and even the sulfite,

have either been suggested or produced to a lim-

ited extent. Schmidt (1857) wrote that basic lead

chloride (patent Bleiweiss) was actually manufactured for a time in Germany. Interestingly, results

reported by Winter (1981) suggest that the basic

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Standing at a Virginal and no. 2568, A Young Woman Seated at a Virginal. In both cases the lead white is mixed with calcium carbonate (identified by Hermann Kühn and Joyce Plesters). Similar results have been obtained by x-ray diffraction for the ground layer in Carel Fabritius's Self Portrait, National Gallery, London, no. 4042 (Ashok Roy, private communication) and in paint and ground layers of pictures by Rembrandt (Bomford et al., 1988). Van de Graaf (1962) in another publication quoted an Italian author, Armenini-writing in 1586, who said that Dutch painters mixed gypsum with one-third lead white in grounds. Since this seems contrary to known Dutch tradition, Van de Graaf was careful to say that gypsum was presumably used by Dutch painters working in Italy. We can conclude that various kinds of lead white or admixtures of lead white with other materials may occasionally be found in paintings. In the nineteenth century, commercial lead white grounds seem to have been commonly extended with kaolin, barytes, and so on.

Source

Although the basic carbonate of lead occurs naturally as the rare mineral hydrocerussite, its counterpart, the paint pigment lead white, has been produced artificially since early historical times (Caley, 1946). Theophrastus (Caley & Richards, 1956), Pliny (Bailey, 1932), and Vitruvius (Morgan, 1926) all described its preparation from metallic lead and vinegar. The same method was probably used in China as early as 300 B.C. (Needham, 1976); some details of the history of lead white preparation in China are given by Sheng (1983). It is one of the oldest synthetically produced pigments.

Preparation: Manufacture

Until recently, lead white was made by the "Dutch" or "stack" process which, so far as we know, differs little in principle from the method used in classical or medieval periods. Metallic lead in the form of strips or "buckles" (fig. 1) was exposed from one to three months in specially made clay pots which had a separate compartment in the bottom to hold a weak solution of vinegar (acetic acid). The pots were stacked in tiers in a shed with fermenting horse manure or waste tan bark, which produced both heat and carbon dioxide. The combined action of acetic vapors, carbonic acid, and heat slowly transformed the exterior of the lead to white basic lead carbonate. The



Fig. 1 Corroded lead "buckle" made in the "old Dutch" or "stack" process for manufacturing lead white. Courtesy, National Lead Company, Philadelphia. Photo: Raymond A. Schwartz.

flaky product was scraped from the surface and after washing, drying, and screening was ground directly in linseed or other drying oil. Unreacted lead was returned to the fermenting pots until eventually consumed. Harley (1982) noted that lead white was manufactured in England in the seventeenth century; in 1622 a monopoly was granted for making both white and red lead. She described a number of variants of the stack process. Both she and Thompson (1936) mentioned that some of the early recipes call for total immersion of the lead in vinegar or suspension over vinegar in closed pots so that only lead acetate could be produced in the first step. Carbonation apparently was done later by roasting the initial product

In the late eighteenth century a purer and whiter product called Krems white (Cremnitz white) was produced in Austria, but it required a longer period for the transformation. Other improvements were made in the early nineteenth century (Kühn, 1967).

Today the lead white of commerce is produced by more rapid chemical processing. All methods have been described in detail in many sources.



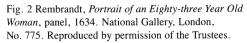




Fig. 3 X-radiograph of the Rembrandt portrait shown in fig. 2. Note the high absorbance for x-rays of the lead white in the sitter's ruff, face, and headdress, which appear as light areas in the radiograph.

History of Use

Lead white is the most important of all lead pigments and, not overlooking the special uses of lime white in wall painting, it is safe to say that, historically, it is the most important of all white pigments. It was the only white pigment used in European easel painting until the nineteenth century. It is mentioned in almost all of the source materials and catalogue lists of pigments from ancient times to the present. The monopoly in lead white production was not broken until the nineteenth century when zinc oxide became a competitor. In the twentieth century it has been extensively replaced by titanium dioxide, which is superior to lead white in some properties.

Since white in a painting is the equivalent of light in nature it has served to delineate form; with blue pigments it has produced the tints of skies; with red, the tones of flesh. It was used in underpainting for the modeling of bodies and for highlights. The white linen ruffs and cuffs of personages in Dutch portraits were done in lead white (see fig. 2) as were also the linen collars and wimples of Flemish ladies. Because of its capacity to absorb x-rays, it is the lead white in European

paintings that makes them amenable to x-radiography (see fig. 3). Lead white was also used occasionally on wall paintings and even in tempera paintings on paper and silk in early periods in China and Japan (Winter, 1981), although lime white produced from calcination of shells of mollusks seems to have enjoyed wider use there (see chapter 9).

Relationship to Media

Lead white has been used in a variety of media. Most of the lead white of European paintings was ground in vegetable drying oil, but there are many examples of early Italian panel painting in which the pigment was used in egg tempera. According to Eibner (1930), only linseed and walnut oil were used in the Middle Ages and poppy oil has been used specially for artists' purposes since the seventeenth century. Linseed oil has the best drying properties. The drying of oil is a complex process and is known to be accelerated by mixture with lead white and some other metallic compounds. The product, when thoroughly dry, is a hard, resistant film which is tougher, more resistant, and less likely to swell in organic solvents than most

other oil-pigment mixtures. This has commonly been attributed to lead soap formation by interaction with linseed oil fatty acids (Oil and Colour Chemists' Association, 1966). Lead soap formation is perhaps the reason for the superior condition of flesh tones in old oil paintings.

Because of its high refractive index, the hiding power of lead white, even in oil, is high (figs. 4 and 5). A special feature of lead white is its low oil-absorption index. It requires only 9 to 13 ml of oil to make a workable paste with 100 g of lead white. In oil, the medium is the continuous phase; hence, the particles of white are completely enveloped. Lead white has also been used with aqueous media such as egg volk and whole egg (egg tempera), gum arabic (watercolor), and with animal glue—the traditional medium of the Chinese and Japanese painters. It was used in the encaustic (wax) technique employed with the Fayum mummy portraits of Ptolemaic times in Egypt. In rare instances it was used in true fresco technique but often with unfortunate results (Augusti, 1949; Kühn, 1967; Matteini & Moles, 1981).

Particle Characteristics

Lead white is made up of finely divided rounded particles fairly uniform in size, varying from 1 to 2 μ (Dunn, 1973). Individual grains at magnification c.1,000x are often tabular and hexagonal in outline (figs. 6 and 7), the morphology being most clearly seen in a scanning electron micrograph at higher magnification (fig. 8). For comparison, the particle form of lead carbonate is shown in figure 9. Further photomicrographs of various crystalline forms of modern basic lead carbonate have been published by Feller (1972), and of so-called "pearlescent" or nacreous lead white (Feller et al., 1971).

Optical Characteristics

The pigment particles (crystals) are strongly doubly refractive: $\varepsilon = 1.94$; $\omega = 2.09$ (Larsen & Berman, 1934). The optical transmission curve of lead white was measured by Stutz (1925).

Chemical Properties

The dry pigment is readily soluble in dilute nitric and acetic acid with release of carbon dioxide gas. However, if the sample of lead white is very small, or if the particles are thoroughly encased in medium—especially dried oil—there may be little or no effervescence. With dilute nitric acid after slow

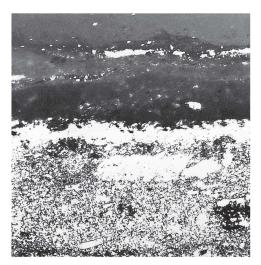


Fig. 4 A thin section of a sample of white paint from Rubens' *Descent from the Cross*, Cathedral at Antwerp, as it appears microscopically by transmitted light. It shows the great opacity of the multiple lead white layers in the upper portions as compared with the transparency of the chalk preparation layers beneath. Photomicrograph 204x. Courtesy J. Thissen, Institut Royal du Patrimoine Artistique, Brussels.

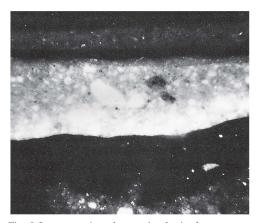


Fig. 5 Opaque section of a sample of paint from shadowed area of flesh of hand of a self-portrait by Rembrandt (signed and of c.1640, private collection, England). The section shows all layers down to, but excluding, the canvas. The thick whitish layer in the middle consists principally of lead white and contains coarse white grains, consisting of large aggregates of pigment particles, which occur in the "old Dutch" or "stack" process of manufacture. 74x. by reflected light. Photo: J. Plesters, National Gallery, London.

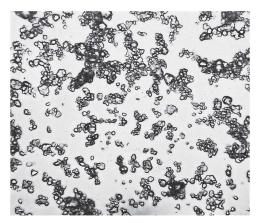


Fig. 6 Particles of lead white mounted in Canada balsam, n = 1.54. 864x by transmitted light. Photo: W. T. Chase.

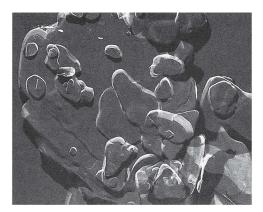


Fig. 7 Electron micrograph (shadowed replica) of the same pigment as shown in fig. 6. Magnification 13,440x. The general hexagonal shape of the particles can be noted. Courtesy Kenneth M. Towe, Department of Paleobiology, Smithsonian Institution.

evaporation, characteristic highly refracting octahedra of lead nitrate, Pb(NO₃)₂, may be observed (fig. 10); on more rapid evaporation, characteristic dendritic crystals are formed, often as square lattices (figs. 11 and 12). With dilute hydrochloric acid, a particle of lead white is directly enveloped with a crust of white lead chloride (PbCl₂), which is much less soluble at room temperature than is lead nitrate. When the pigment is dissolved in dilute nitric acid, and hydrochloric acid is subsequently added, the lead in the solution precipitates in the form of tong-shaped and cross-shaped crystals of lead chloride (fig. 13). Both of these reactions serve for the provisional identification of lead. With dilute sulfuric acid there may be little

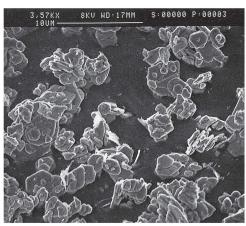


Fig. 8 Scanning electron micrograph of particles of lead white pigment (basic lead carbonate). Gold-coated, printed at 2,400x. Photo: A. Roy.

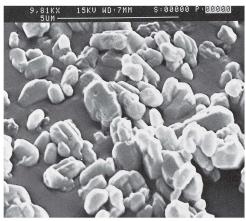


Fig. 9 Scanning electron micrograph of particles of neutral lead carbonate, PbCO₃. Gold-coated, printed at 6,377x. Photo: A. Roy.

apparent reaction because of the formation of fine granular insoluble lead sulfate. Lead white turns yellow when heated to a low temperature because of the formation of massicot (lead monoxide, PbO); higher temperatures convert massicot to litharge and eventually to red lead (minium, Pb₃O₄).

Permanence and Compatibility

Although a carbonate, and hence reactive to acids, lead white has a remarkable record for permanence. It is unaffected by light. When applied in watercolor technique, however, as in the highlights of old master drawings, traces of hydrogen sulfide in the air cause lead white to turn black.

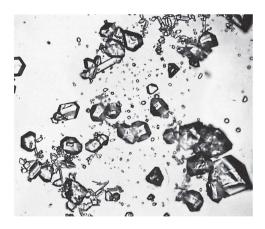


Fig. 10 Octahedral crystals of lead nitrate produced by reaction of dilute nitric acid with a particle of lead white paint from a painting by James A. McNeill Whistler, *The Music Room*, Freer Gallery of Art, No. 17.234. Wet mount after slow evaporation of the test drop: without cover glass; transmitted light 155x. Photo: W. T. Chase.

Augusti (1949) described the blackening of lead white used on mural paintings in Italy, and Plenderleith (1956) has an illustration of a drawing in which lead white highlights have blackened, together with the same drawing after treatment with hydrogen peroxide to convert the black PbS to white PbSO₄. More recent work on discolored white pigment found on wall paintings has indicated that brown lead dioxide (PbO₂) may be formed (Matteini & Moles, 1981), but the mechanism has not been firmly established. Oxidation by microorganisms is a possible route (Petushkova & Lyalikova, 1986). It has also been shown that reconversion of lead dioxide to lead white may be accomplished using hydrogen peroxide in acetic acid solution (Giovannoni et al., 1990), and that this reagent is successful in practice for wall paintings (Koller et al., 1990). Lead white locked in a drying oil film and protected with varnish endures for centuries without blackening; witness the white collars and cuffs in Dutch portraits (fig. 2). Although lead white is theoretically incompatible with sulfide pigments, and should form black lead sulfide in contact with them, no glaring examples can be cited. Flesh tones, lead white tinted with red mercuric sulfide (vermilion) especially in oilmedium, have stood for centuries without change; as similarly have mixtures with ultramarine in skies and draperies. Lead white mixed with cadmium sulfide also seems unaffected. There might be some question, however, about lead white and

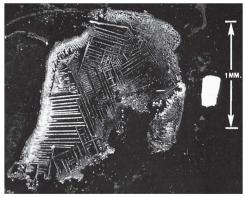


Fig. 11 The small size of samples needed for microchemical tests is shown here. On the right, a particle of lead white in oil paint from a painting by James A. McNeill Whistler, *The Music Room* (Freer Gallery of Art, No. 17.234), measures about 0.3 mm in longest dimension. Directly on the left, a lattice of lead nitrate crystals formed by the action of a single drop of nitric acid applied to a second particle of approximately the same size is shown. The lacy filaments on the periphery of the test drop are the residue of drying oil that served as the pigment binder. Dry preparation by reflected light, 28x. Photo: W. T. Chase.

orpiment mixtures, although in several examples identified at the National Gallery in London, no visible interaction seems to have taken place.

Microchemical Tests

Preliminary indications of the presence of lead, when observing the behavior of a sample in dilute nitric and hydrochloric acids, have been mentioned. More specific reactions for lead, which may be applied successfully to tiny samples of paint barely visible to the naked eye, are as follows:

Test with Potassium Iodide to Form Pbl₂

The residue of lead nitrate from the nitric acid treatment is taken up with a drop of water (some prefer a drop of dilute acetic acid) and a tiny crystal of potassium iodide (KI) is added. PbI₂ precipitates immediately in thin bright yellow scales or hexagonal plates (see figs. 14 and 15) which flash and scintillate from Brownian movement. This initial tumbling of the crystals may appear green or brown by transmitted light. There may be some iridescence in reflected light. As a precaution, the test particle of KI must not be too large because PbI₂ is soluble in an excess of that reagent. Too

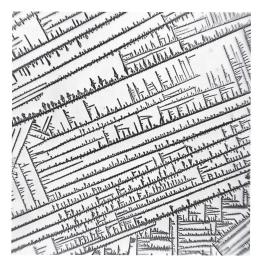


Fig. 12 Lattice of lead nitrate crystals produced from the evaporation of a test drop of dilute nitric acid applied to a particle of powdered lead white. Dry preparation on a microscope slide by transmitted light, 57x. Photo: Elisabeth West FitzHugh.

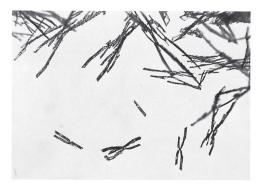


Fig. 13 Crystals of lead chloride (PbCl₂) produced by adding a small drop of dilute hydrochloric acid to a test drop of lead nitrate which previously was formed by the action of dilute nitric acid on a particle of lead white. Wet mount without cover glass; transmitted light 64x. Photo: Elisabeth West FitzHugh.

much HNO₃ will decompose KI with release of elemental iodine. According to Short (1940), the limit of identification is 0.0005% lead acetate (5 ppm).

Test with Copper Acetate and Potassium Nitrite to Form K₂PbCu(NO₂)₆

This is identical with the "triple nitrite" test for copper described under azurite (chapter 1), except that the reagent is made of 0.5% copper acetate and 0.5% sodium acetate in 1% acetic acid. A single fragment of solid potassium nitrite, KNO₂,



Fig. 14 A test precipitate of lead iodide formed from the residue of lead nitrate shown in fig. 11. The yellow precipitate of glistening hexagonal platelets of PbI₂ were formed when the residue was taken up in a single drop of water and a tiny crystal of potassium iodide added. In the center surrounding the incompletely dissolved crystal of KI there is a dark zone where the concentration of reagent is too high for formation of the PbI₂. Wet preparation by reflected light, 30x. Photo: W. T. Chase.

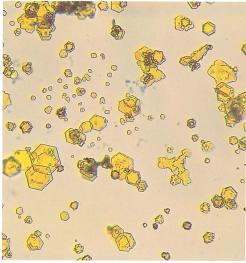


Fig. 15 Crystals of lead iodide, wet preparation with cover glass viewed by transmitted light, 183x. Photo: W. T. Chase.

is then introduced into the solution. When lead is present, it immediately precipitates as the triple salt in the form of brown and black cubic crystals (see fig. 9, chapter 1). This is the preferred test for lead in the Laboratory of the Institut Royal du Patrimoine Artistique in Brussels.

Criteria for Certain Identification

High density and high opacity of the white pigment (figs. 4 and 5), solubility in dilute nitric acid with fast or even slow release of bubbles of carbon dioxide, and a strongly positive test for lead are ordinarily sufficient evidence to establish, with confidence, the presence of lead white. A specific test for the carbonate radical is usually not necessary unless some other anion is suspected. Instru-

Fig. 16 X-ray diffraction powder patterns of lead-based whites.

A. Lead white. Commercial dry pigment. F. Weber Co., Philadelphia, 1934.

B. Lead white. White pigment on Japanese painting, Ukiyo-e School, style of Katsushika Hokusai (1760–1849). Freer Gallery of Art, No. 03.125.

C. Laurionite mineral, Pb(OH)Cl, Laurium, Greece. Department of Mineral Sciences, Smithsonian Institution, specimen 93774.

D. Lead sulfate. Browning. Freer Gallery of Art Technical Laboratory pigment collection. Photographs not to be used for measurement purposes. XRD patterns by Elisabeth West FitzHugh. mental methods of detection or quantitative estimation described below may have special uses.

Emission Spectrometric Analysis of Lead

Lead is readily detected spectrometrically. Prominent lines in the visible range are 6001.8 and 4057.8 Å (Peterson & Jaffe, 1953); in the ultraviolet they are 2873.3, 2833.1, 2802.0, and 2614.2 Å; and sensitivity is 0.01% (Waring & Annell, 1953). In the spark spectrum, other useful lines include 3683.5 and 3639.6 Å (Handbook of Spectroscopy, 1974) and the absolute limit of detection with the laser microprobe is $4.5 \times 10^{-10} \text{ g}$ (Moenke & Moenke-Blankenburg, 1973). Neither the binder, vehicle, nor other anions and cations interfere with the lead spectrum. Research at the Doerner Institute in Munich has indicated that lead white in paintings always contains characteristic impurities that can be estimated spectrometrically. The most significant impurities are the elements copper and silver, and sometimes tin. Comparison of the line intensities of copper and silver in many dozens of samples points to a different coppersilver ratio depending on whether the paintings came from the Netherlands or Italy. It has also been established by emission spectrum analysis that the more recent lead white from the late nineteenth or twentieth century contains, as a rule, substantially smaller traces of copper and silver (see also Neutron Activation Analysis). Semi-

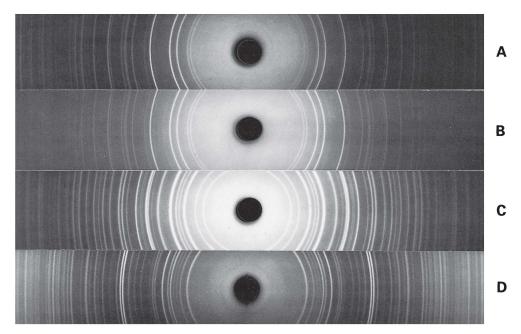


Table 1 X-ray Diffraction Data for Lead White

Paint Sample: White of Headdress from Rubens' Samson and Delilah (National Gallery,

$2PbCO_3.Pb(OH)_2^{a,b}$			London, N	lo. 6461) ^{c.d}		$PbCO_3$	b,e
d(Å)	I	d(Å)	I	d(Å)	I	dÅ	I
4.47	60	4.47	50			4.427	17
4.25	60	4.23	50			3.593	100
3.61	90	3.60	100	3.50	50	3.498	43
3.29	90	3.28	80	3.07	30	3.074	24
2.715	20	2.71	20			2.589	11
2.623	100	2.62	100	2.52	20	2.522	20
2.491	30	2.49	50			2.487	32
2.231	50	2.22	50			2.081	27
2.120	30	2.12	30	2.01	20	2.009	11
2.099	20	2.09	40	1.93	20	1.933	19
2.046	30	2.04	20			1.859	21
1.884	20	1.88	10				
1.856	30	1.85	60				
1.696	40	1.70	50				
1.649	20	1.65	10				
1.613	30	1.61	10				
1.584	20	1.58	50				
1.530	30	1.53	20				
1.513	20	1.51	20				
1.485	20	1.48	10				
1.309	30	1.31	20				
1.292	30	1.29	10				
1.251	30	1.25	10				

a. JCPDS Powder Diffraction File 13–131 (Courtesy of JCPDS International Centre for Diffraction Data).

quantitative spectrographic analysis for trace elements, particularly copper and silver, with the laser microprobe has been used to distinguish different metallurgical processes for the production of lead as a source for lead white (Kossolapov & Sizov, 1984).

X-ray Diffraction Analysis

This is a certain and easy means of confirming the presence of lead white and of estimating its purity. Debye-Scherrer powder patterns of pigment samples in micro quantities can be made with a cylinder camera by picking up a few pigment or paint particles on a greased glass filament. The spacings and intensities of both the basic and the

neutral carbonate of lead, taken from the *JCPDS Powder Diffraction File* are shown in table 1 with data for a sample of lead white from a Rubens painting. Typical Debye-Scherrer patterns are shown in figure 16.

Using x-ray diffraction data, Keisch (1972) has demonstrated that several possible phases may be present in manufactured lead white and that the various forms yield unique diffraction lines that allow their proportions to be estimated. The compostion may be a guide to the origin and date of the sample.

Many of the samples of lead white taken from a range of paintings in the National Gallery, London, have been found by x-ray diffraction to contain significant proportions of neutral lead carbon-

b. Only lines with an intensity greater than 10 are given.

c. 114 mm Debye-Scherrer camera, CuK α radiation, 3 hours, 40 kV, 35 mA, line intensities visually estimated (A. Roy).

d. See Plesters, 1983.

e. *JCPDS Powder Diffraction File* 5–147 (Courtesy of JCPDS International Centre for Diffraction Data).

f. Lines in sample due to neutral lead carbonate.

ate in addition to the basic form (Ashok Roy, private communication).

Neutron Activation Analysis

This special method for determining trace impurities has become important in recent years. Preliminary investigations indicate that it is sometimes useful for giving information relating to both the general region of origin and the age of a painting on which white lead occurs. By using samples (of the order of l mg weight or less) of lead white from paintings dating back to about A.D. 1500, irradiating them in a neutron flux in a nuclear reactor, carrying out the necessary chemical separation of elements, and finally measuring the half-lives of isotopes produced, Houtman and Turkstra (1965) reported that lead white produced before 1850 had appreciably higher contents of silver, copper, mercury, manganese, and chromium. After that date the content of those same elements was much lower or even nearly nonexistent. Zinc and insoluble antimony, nearly absent before 1850, increased greatly after that date. The nineteenthcentury change is explained by changes in the treatment of lead ores and in manufacturing processes. Lux and Braunstein (1966) in Munich claimed to have confirmed the observations of Houtman and Turkstra in respect to the low-silver and copper content and high-zinc content of twentieth-century lead white, but they found there are appreciable differences in the impurities of copper, silver, manganese, and antimony in samples of lead white from Dutch paintings as compared with Venetian paintings going back many centuries. However, unambiguous correlation of trace element composition with period of manufacture is not straightforward (Lux et al., 1969). These differences, which were also confirmed in emission spectrometric analysis by Kühn (1967), apparently do not relate to production processes, but to differences in amounts of these trace elements in different sources of lead ore. More recently, Lux et al. (1980) have compared lead white from an eighteenth-century painting with the modern pigment for a greatly extended range of metallic trace impurities by neutron activation analysis using a number of sample weights to ascertain whether homogeneity of the sample will influence the results. The same workers ascribe an Italian origin for lead white in a Rubens painting on the basis of silver and antimony concentrations.

New work in France using proton induced x-ray emission analysis (PIXE) has shown significant

variations in trace element content from the sixteenth century to the present (Nens et al., 1984), and is also in accord with the results of Houtman and Turkstra (1965). High levels of zinc are sometimes noted in samples from the mid-nineteenth century, but this diminishes markedly in lead white produced after the 1960s. An overview of the state of present studies is given by Lancelot et al. (1987).

Analysis of the Natural Radioactivity of Lead

Keisch and coworkers in Pittsburgh (Keisch et al., 1967; and Keisch, 1970a) have shown that it is possible to differentiate between "old" and "modern" lead white by estimating the amount of the radioactive isotope 210Pb. The basic theory is that when lead is extracted from its ore, the 210Pb is chemically separated from uranium, radium, and other members of the radioactive series, thus disturbing the radioactive equilibrium. The radioactive 210Pb, which has a half-life of twenty-two years, is no longer supported by its relatively long-lived ancestor ²²⁶Ra, hence decay continues until 210Pb activity is once more in equilibrium with the much smaller quantity of radium surviving the chemical fractionation process. The best method of estimating the concentration of 210Pb involves determining the concentration of its alpha-emitting descendant, 210Po. 226Ra is also determined. When the concentration of 210Po in disintegrations per minute (dpm) is greater than the rate of disintegration of ²²⁶Ra, the lead white is of relatively modern manufacture; but when the dpm of 210Po and of 226Ra are equal within the uncertainties of the measurement, the lead white is much older. The method requires about 5 to 25 mg of lead white, because of the low concentration of natural radioactivity encountered, but can be used to distinguish between lead that is less than approximately 100 years old and lead that is greater than approximately 150 years old.

Mass Spectrographic Analysis

The technique of isotope analysis outlined by Brill and Wampler (1967) and Brill et al. (1970) may prove useful in determining the geographical sources of the lead used in making lead white pigments. The problem is also discussed by Keisch (1970b) who has published the expected isotope ratio ranges for ²⁰⁶Pb/²⁰⁴Pb from a number of different origins. Some preliminary isotope studies also by Keisch on samples of lead white and red

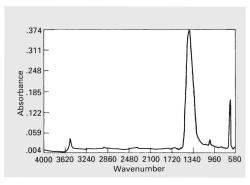


Fig. 17 Infrared absorption spectrum (FTIR) of lead white recorded by transmission. Strong absorptions at 1405 cm⁻¹ (broad) and 681 cm⁻¹ (sharp) as well as a weaker feature at 1046 cm⁻¹ (sharp) are produced by the carbonate function; the hydroxyl group absorbs weakly at 3538 cm⁻¹.

Spectrum courtesy of Jennifer Pilc.

lead from medieval Norwegian works have been reported by Plahter (1976) and comparison made with the results of trace element analysis by neutron activation (Steinness, 1976).

Infrared and Raman Spectrometry

One of the authors (Kühn, 1967) published the infrared spectrograms of both normal and basic lead carbonate standards and also of samples of lead white from old paintings; in one case basic carbonate, in the other, a mixture of normal and basic carbonate. Only 50 to 100 μg are required for the tests. Hunt et al. (1950) reported a similar infrared absorption spectrum of lead white using particles less than 5 μ in diameter deposited on a conventional rock-salt window. Afremow and Vandenberg (1966) published data in the mid-infrared region on several white pigments and extenders including basic lead carbonate. The infrared spectrum is shown in figure 17.

More recently infrared and Raman spectra were given by Brooker et al. (1983) for both hydrocerussite and cerussite, with assignments of the bands and certain structural correlations. For lead white (hydrocerussite), strong carbonate stretching vibrations occur at 1400, 1045, and 693–683 cm⁻¹ in the infrared, and at 1363 and 1053–1049 cm⁻¹ in the Raman spectrum. The OH stretch is recorded as a weak band around 3530 cm⁻¹ in each spectrum. PbO modes occur as mediumintensity absorptions in the infrared at 392 cm⁻¹, and 415 cm⁻¹ in the Raman spectrum. For neutral lead carbonate (cerussite), absorptions attribut-

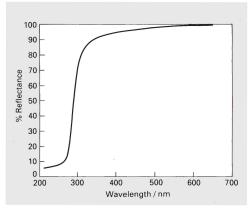


Fig. 18 Spectral reflectance curve for lead white. After T. C. Patton (ed.), *Pigment Handbook*, vol. 1 (New York, 1973), p. 72.

able to carbonate are present at 1435–1400, 1052, 838, and 682 cm⁻¹ in the Raman spectrum (Brooker et al., 1983).

X-radiography

Opacity to x-rays of white-painted areas in paintings may indicate the presence of lead white (fig. 3). All-over uniform opacity sometimes reveals the presence of a lead white ground or relining adhesive. It has been pointed out by Ainsworth et al. (1982) that paintings that yield poor or valueless x-radiographs because of thick primings of lead white, may be suitable subjects for neutron autoradiography. Because lead white absorbs x-rays, areas on the photographic negative opposite lead white, when viewed over a light box, are seen as light or transparent areas. De Wild (1929) gave the mass absorption coefficient of lead white in oil as 72.7 as compared with 37.9 for zinc oxide in oil. High x-ray absorption in paintings is not proof of lead white, however, because other pigments such as vermilion, mercuric sulfide (HgS) (see chapter 7), and lead-tin yellow, (Pb₂SnO₄) (see chapter 4), also have high x-ray absorption; moreover, x-ray absorption depends on the thickness of lead white paint and other factors.

Reflectance Spectrophotometry

Barnes (1939) gave a color reflectance curve for lead white: the dominant wavelength is 576.7 nm, the relative brightness is 87.3%, and the excitation purity is 4.1%. CIE 1976 L*a*b* chromaticity calculations give L*=97.1, $a^*=-0.206$, $b^*=2.22$ (David Saunders, private communication).

The ultraviolet reflectance in the range 310–400 nm is high, falling rapidly below 310 nm, and strongly absorbing ultraviolet light in the range below 270 nm; in the near infrared, the reflectance is high (Dunn, 1973) (see fig. 18).

X-ray Spectrometric (X-ray Fluorescence) and Electron-Probe Microanalysis

Some of the chief lead lines are PbK $\alpha_{1,2}$ 75.0 and 72.8 keV, PbL α_1 10.6 keV, and PbL β_2 12.6 keV (*Handbook of Spectroscopy*, 1974). For the L lines the best count-rates are obtained with a ¹⁰⁹Cd source (Hanson, 1973).

Lead white has been detected by the electronprobe microanalyzer in a paint sample from Hendrik ter Brugghen's *The Lute Player* (National Gallery, London, no. 6347) (Hornblower, 1963).

Notable Occurrences

In Western Paintings

Lead white has been used in painting so widely and for such a long time that it would be tedious to list all occurrences. De Wild (1929) listed over eighty Dutch paintings dating from the mid-fifteenth to the mid-nineteenth centuries on which it occurs. One of the authors (Kühn) identified it on some 600 paintings in the Bayerischen Staatsgemäldesammlungen, Munich.

- (a) On a Fayum portrait (Egypt, first to third centuries A.D.) at Goucher College, Baltimore, Maryland. Reported by Stout (1932).
- (b) On a Fayum portrait (second century A.D.) in the Martin-von-Wagner-Museum, Würzburg (Kühn, 1967).
- (c) In Pablo Picasso's *The Three Dancers* (Tate Gallery, London, no. T729), painted in 1925. Identification by x-ray diffraction (Ashok Roy).
- (d) An interesting occurrence of lead white, not in an oil painting, is as the white pigment in the paint layers of the Raphael cartoons for the Sistine Chapel tapestries (cartoons in the collection of Her Majesty the Queen, on loan to the Victoria and Albert Museum, London). Although in an aqueous medium (a comparatively high proportion of animal glue), the lead white pigment—whether used alone or mixed with other pigments—shows no appreciable sign of discoloration by conversion to black lead sulfide even after more than a century in the London atmosphere. Identification by Joyce Plesters.

In Oriental Paintings

- (a) In Japanese objects decorated with oil paint from the Shôsôin, Nara (A.D. 756). In this connection it is interesting to note that in A.D. 692 the monk Kanshô won a prize for preparing white lead. Reported by Yamasaki (1966).
- (b) On paintings from Dun-huang in western China, dated to the ninth or tenth century A.D. Reported by Warner (1938).
- (c) In a Chinese scroll painting of Avalokiteśvara with two attendant deities, dated A.D. 968, supposedly found at Dun-huang, now in the collection of the Freer Gallery of Art (no. 30.36) and in another painting of approximately the same provenance and date (no. 35.11).
- (d) In Japanese wall paintings in the Daigo-ji Pagoda (A.D. 951). Reported by Yamasaki (1959).
- (e) In the E-ingakyô Sutra (Illustrated Sutra of Causes and Effects), early eighth century A.D.; also in the Genji Monogatari Emaki (Scroll of the Tale of Genji), first half of the twelfth century. Both reported by Yamasaki (1954).
- (f) In a pair of Japanese handscrolls of the Kamakura period (fourteenth century) in the Freer Gallery of Art, Washington (nos. 58.11 and 59.13).
- (g) In a Japanese painting of the Bodhisattva Fugen now in the Freer Gallery (no. 63.6) dating from the twelfth century. See also Yanagisawa (1962).
- (h) On some of the Chinese silk paintings from the cave "Halls of the Thousand Buddhas" at Dunhuang, now in the Dr. M. Aurel Stein Collection at the British Museum. Examples have so far been identified on no. 1919-1-1-099, Seven Treasures of the Birth of Buddha; no. 1919-1-1-0124, Vajrapini; and no. 1919-1-1-05, Avalokiteśvara (dated A.D. 864). Identification by Joyce Plesters.

Objects of Art Other than Pictures

- (a) The ground layer of a Chinese polychromed terra cotta tomb figure of the Tang dynasty was found by x-ray diffraction to be mainly neutral lead carbonate containing a low content of the basic carbonate, the reverse proportions usually found in samples from European painting (Victoria and Albert Museum, London, no. C879–1936). Reported by Ashok Roy.
- (b) In underlayers bound in egg medium on thirteenth-century polychromed stone figures at Wells Cathedral, Somerset, England. Microchemical and spectrographic analysis by Ashok Roy.

(c) As a white pigment and opacifying agent mixed into beeswax in several wax sculptures in the collection of the Victoria and Albert Museum, London. These are: Giuliano Zumbo (1655–1701), wax tableau depicting an *Allegory of Death*; wax relief profile portrait (English), second quarter of the nineteenth century; English nineteenth-century wax bust. The lead white was detected both chemically and by x-ray fluorescence analysis by Joyce Plesters and metal salts of wax acids were detected by J. Mills using infrared absorption analysis. Reported by Joyce Plesters.

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4

Lead_Tin Yellow

HERMANN KÜHN

Current Terminology

English: lead-tin yellow French: jaune de plomb étain German: Blei-Zinn Gelb Italian: giallo di piombo-stagno Spanish: amarillo de plomo-estano

Obsolete Terminology

Although lead—tin yellow frequently occurs in European painting before the eighteenth century, there is little certain evidence of its use from the older literature on painting techniques. The earliest recipe for a yellow pigment from lead and tin was found in the Bolognese manuscript (deduced by Merrifield [1849, vol. 2, p. 529] to be of the first half of the fifteenth century) under the following recipes:

Rp. 272. A fare vetrio giallo per patre nostre o ambre.— Tolli piombo lb j. stagno lb doj. et fundi et calcina et fa vetrio per patrenostro. [To make yellow glass for paternosters or beads: Take of lead 1 lb., of tin 2 lbs., melt and calcine them, and make glass for paternosters.]

Rp. 273. A fare zallolino per dipengiare.—Havve lb doi de questo stagno et piombo calcinato et doi lb de questo vetrio da patrenostrj et doi lb et ½ di minio et mezza lb de rena de valdarno sotilmente pista et mecti in fornace et fa affinare et sera perfecto. [To make giallolino for painting: take 2 lbs. of this calcined lead and tin, that is 2 lbs. of this glass for paternosters, 2½ lbs. of minium, and ½ lb. of sand from the Val d'Arno pounded very fine; put it into a furnace and let it fine itself, and the color will be perfect.]

Giallolino (zallolino) or giallorino mentioned in recipe 273 means a yellow of pale color which is, so to speak, expressed by the diminutive form -lino or -rino attached to giallo (yellow). Merrifield (1849) stated that the giallolino always men-

tioned in Italian manuscripts is identical with the massicot of the northern manuscripts. She drew her conclusion from the fact that in southern manuscripts, only giallolino and not massicot is used, but in northern manuscripts only massicot and not giallolino is mentioned. The one preparation of massicot described in a sixteenth-century northern source involves calcination of lead and tin, followed by the addition of minium (red lead) with further lengthy heating (Plesters, 1983); this process must surely have produced a lead-tin oxide. However, Haydocke (1598) published Lomazzo's treatise in English, translated giallolino into "massicot or general": "the matters of yeallowe, are yeallowe of the Flaunders fornace and of Almany, commonly called masticot and generall." The use of both terms, massicot and general, seems to be peculiarly English, while the Spanish had only génuli and Flemish had massicot (N. Eastaugh, private communication, 1986). Seventeenth-century painting treatises from Spain and Portugal edited and translated by Veliz (1986), do, however, indicate at least two separate varieties of leadbased yellow, one of which (hornaza or ornacha) was a product of the glassmakers' furnace. Hornaza may therefore be equivalent to the pigment described in the Bolognese manuscript. The other yellow called génuli, genoli, or machim, was quite distinct and seems to have been available in different shades. Interestingly, in a sixteenth-century English documentary source there is a clear distinction between massicot and general. For example, in The Ways how to lymme by John Gwillim, a price list of pigments gave them as separate items, with the former twice the price of the latter. Whether these two pigments are to be identified as the distinct varieties of lead-tin yellow now

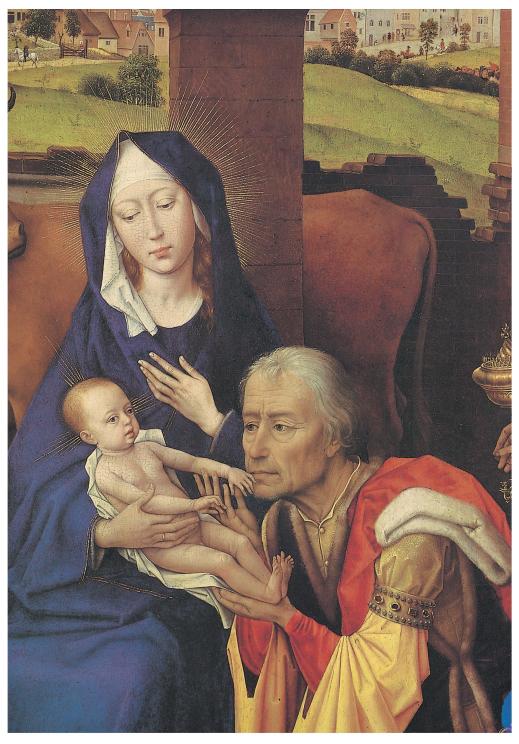


Fig. 1 Detail from Rogier van der Weyden's *Columba Altarpiece*, BSTG No. WAF 1189. The pigment for the king's sleeve is lead–tin yellow.

known to have been used in painting is difficult to establish.

Van Helmont, a seventeenth-century physician, mentioned that tin affords to painters a yellow color, which they call *masticot* (Harley, 1982).

The following points of evidence lead us to suppose that both the *giallolino* (*giallorino*) mentioned in Italian literary sources and the massicot (masticot) of the northern manuscripts are identical with lead–tin yellow (Kühn, 1967):

- (a) Yellow lead oxide (PbO), presently designated as massicot, has only very rarely been found in any painting made between the thirteenth and twentieth centuries (see also Date and Circumstances of Rediscovery).
- (b) We have, however, in Munich, identified lead—tin yellow in 154 paintings of established date, provenance, and authorship, and in four polychrome sculptures (see Notable Occurrences). Other laboratories report similar findings.
- (c) In our investigations of Italian paintings we have not yet found any other unknown pigment which could be related convincingly to the *giallolino* or *giallorino* frequently mentioned in Italian manuscripts. So far, our earliest examples of Naples yellow as a pigment come from the seventeenth century.
- (d) In analyzing several lead oxide samples from old pharmacies, we have established that samples designated *Plumbum oxydatum fusum*, *Pulvis Lithargyri levigatum*, and *Bleiglätte* are in fact yellow lead oxide (PbO), while samples designated *Massikot* are lead–tin oxide (2PbO.SnO₂) with lead oxide (PbO) admixtures.

Composition and Structure

There are, in fact, two kinds of lead-tin yellow, here designated as types I and II. The more frequently used type I is lead-tin oxide of the composition Pb₂SnO₄.

Type II is a second variety of lead—tin oxide that may contain free tin oxide and additional silicon (Si). Its exact stoichiometric composition is so far unresolved. The x-ray diffraction pattern of type II is close to a yellow lead—tin oxide (see X-ray Diffraction Data), identified by Rooksby (1964) as an opacifier in ancient glasses, and that has been shown to have the cubic pyrochlore type structure. The material was synthesized by doping a preformed Pb₂SnO₄ (type I) with silica and heating the mixture in the temperature range 800°–950°C, resulting in a compound with a molecular formula

that approximates to PbSnO₃, or Pb(Sn,Si)O₃, if allowance is made for the possible incorporation of a small amount of silica. R. J. Davis of the British Museum, Department of Mineralogy (private communication), assumes that PbSnO₃ may be stable only at low temperatures, but it probably decomposes at 800°C or above with the reformation of some free stannic oxide. It may be stabilized by the addition of other elements, so that a formula PbSn₂SiO₇ can be drawn in consideration of Rooksby's material. The structure and composition of type I has been examined by x-ray diffraction (Garnier et al., 1976), neutron diffraction (Gavarri, 1982), and vibrational spectroscopy (Vigouroux et al., 1982). The compound is isostructural with tetragonal lead tetroxide (Pb₃O₄, minium) although it does not undergo the phase transitions exhibited by the latter. In the type I form, lead-tin yellow comprises chains of edgesharing Pb(IV)O₆ octahedra linked laterally by Sn(IV) and Pb(II) atoms, each with a pyramidal arrangement of three O neighbors (see Wells, 1984).

Date and Circumstances of Rediscovery

Although lead-tin yellow was frequently used in European painting before 1750, apparently it was not used after that time. To our knowledge, there is no reference to a yellow pigment consisting of lead-tin oxide in the whole literature on colors from the nineteenth and twentieth centuries up to 1941. About 1940, lead-tin yellow was rediscovered by Jacobi (1941) at the Doerner Institute in Munich while he was carrying out emission spectrometric investigations of samples from paintings, and subsequently it was synthesized in the laboratory. Jacobi's attention was drawn to it because he observed that the samples of the yellow he had investigated always had a high tin content in addition to the lead. In contrast to microchemical analysis, unexpected elements are easily detected by means of spectrometric analysis. Microchemical analysis proves only the presence or absence of those elements for which specific tests are applied. Since, however, lead-tin yellow was unknown to analysis before Jacobi's publication, there was thought to be no reason to carry out microchemical tests for tin. This relates especially to the investigations of De Wild (1929) who identified yellow lead oxide on thirty-nine paintings of the fifteenth, sixteenth, and seventeenth centuries, because he tested only for lead, and also because he could find confirmation of his observation by the term massicot in the literature of painting techniques. Raehlmann (1914), who allegedly found Naples yellow (lead–antimony oxide) on several paintings of the Renaissance period, also restricted himself to the identification of lead; he did not carry out specific tests for antimony. Therefore, it can be assumed with high probability that the yellow pigments recognized as yellow lead oxide by De Wild as well as the samples designated Naples yellow by Raehlmann are actually lead–tin yellow.

History of Use and Terminal Date

The uses of lead—tin oxides as opacifiers for glass and in ceramic glazes are known before 1300. Lead—tin yellow type II has been identified in a late Roman shard (fourth—fifth century A.D.) using x-ray fluorescence (XRF) and x-ray diffraction (XRD) (Lazzarini & Hreglich, 1977), and in various examples of early glass of disparate origin and date, in certain cases in conjunction with a lead—antimony phase (Turner & Rooksby, 1959 and 1961).

As outlined under Obsolete Terminology, it can be assumed that the term *giallorino* (*giallolino*) in Italian manuscripts and the term massicot (masticot) in northern manuscripts both mean lead–tin yellow. According to Merrifield (1849), *giallolino* was mentioned by Cennino, Borghini, Leonardo da Vinci, Lomazzo, and in the Paduan manuscript; massicot was mentioned in the Brussels manuscript by Van Mander, Hoogstraten, De Bie, and Beurs. Masticot is also mentioned in the De Mayerne manuscript (Van de Graaf, 1958) published in 1620. In addition, massicot (masticot) is found in numerous other technical treatises and lists of pigments, a full account of which would take too much space here.

By means of emission spectrometric analysis, lead-tin yellow has so far been identified at the Doerner Institute on 154 paintings (including two examples of wall painting) and four polychrome sculptures (see Notable Occurrences). All paintings on which lead-tin yellow has been identified originated in the time span between about 1300 and 1750 (see figs. 1–4). It was most frequently used in the fifteenth, sixteenth, and seventeenth centuries. In the first half of the eighteenth century it began to occur less frequently. It has not yet been found in paintings of the second half of the eighteenth century and later, although a greater number of paintings from the second half of the

eighteenth and nineteenth centuries have been investigated. Of the few paintings and polychrome sculptures that date before 1300, lead—tin yellow has so far not been found. This is not proof, however, that lead—tin yellow was unknown before 1300, although in works of art before that time orpiment is frequently found.

According to our investigations, lead-tin yellow types I and II were not used for painting after the middle of the eighteenth century, and so its occurrence can be helpful in authenticity studies. Despite this, the appearance of lead-tin yellow might be possible on copies of forgeries produced after about 1941, the date of the rediscovery of the pigment by Jacobi. In recent years, at least one color manufacturer lists true lead-tin yellow as an artist's dry powder color. It is also possible that after about 1750 a painter could have obtained lead-tin yellow from old pharmacy stocks or old pharmaceutic-historical collections.

References to the Occurrence of Lead-Tin Yellow in Paintings

About 1940 Jacobi (1941) identified for the first time lead-tin yellow on German paintings of the fifteenth and sixteenth centuries and also on Netherlandish and Dutch paintings of the sixteenth and seventeenth centuries. A few years later, Gettens (1947) found it on four paintings at the Harvard University Art Museums (Fogg). Coremans et al. (1952) described the occurrence of lead-tin yellow in early Netherlandish painting of the fifteenth and sixteenth centuries. Further examples of leadtin yellow in early Netherlandish paintings of the fifteenth century are mentioned by Sneyers and Thissen (1958) and also by Coremans and Thissen (1961), and in recent years reports on the materials of old master paintings frequently refer to the use of lead-tin yellow.

Relative Frequency of Lead-Tin Yellow I and II on Paintings

With the aid of x-ray diffraction analyses, two kinds of lead-tin yellow have been identified. Paintings and polychrome sculptures, of which x-ray analyses are available, have been marked with "D" under Notable Occurrences. Of the thirty-four works of art marked with "D," in twenty-nine cases lead-tin yellow I and in five cases lead-tin yellow II (under Notable Occurrences designated "D*") have been identified. At the National Gallery, London, of thirty-four samples analyzed by x-ray diffraction, nine



Fig. 2 Detail from Bergognone's Altarpiece: The Virgin and Child with Saints Catherine of Alexandria and Siena, panel, c.1490. National Gallery, London, No.

298. Reproduced by permission of the Trustees. The Child's dress is painted in lead–tin yellow type I.

proved to be type II, and the remainder were type I. These results, although based on a relatively small number of works, show that lead-tin yellow I was used more frequently than lead-tin yellow II, but that type II was generally the earlier pigment. Lead-tin yellow II has been found principally in Florentine, Venetian, and Bohemian paintings. It has been identified, for example, on early Florentine works ascribed to Giotto, and to the di Cione workshop (Gordon et al., 1985; Bomford et al., 1989). Two paintings of the Gonzaga Cycle painted by Tintoretto in Venice have been shown to contain type II. Both paintings can be dated to just before 1579 and belong to the first series of the Cycle. However, in two paintings from the second series of the same group, which

date from 1579/1580, lead-tin yellow I was found. Similarly, in the four Veronese Allegories of Love in the National Gallery, London, dated to the last quarter of the sixteenth century, lead-tin yellow I had been used in one of the series, while type II was present in two of the other compositions (see Notable Occurrences). A paper by Martin and Duval (1990) has explored more fully the history of use in Italy of lead-tin yellows of the two crystallographic types, basing their distinction on the presence or absence of silicon as determined by EDX analysis of samples in the SEM. For approximately one-hundred samples of leadtin yellow, they have shown that lead-tin yellow type I replaced lead-tin yellow type II in Italy during the second quarter of the fifteenth century and

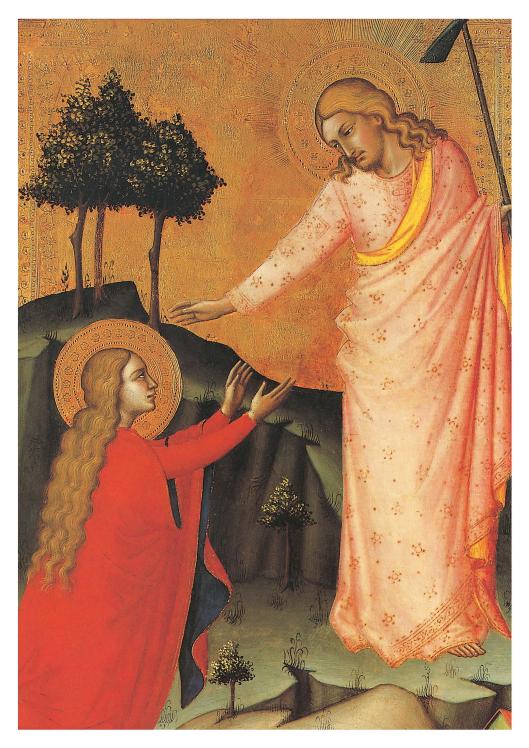
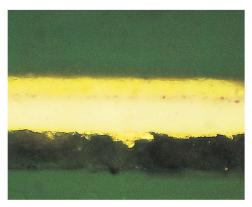


Fig. 3 Noli me Tangere, Master of the Lehman Crucifixion, panel, after 1365. National Gallery, London, No. 3894. Reproduced by permission of the Trustees.

A. The lining of Christ's robe is painted in lead-tin yellow type II.



B. Cross section of the lining to Christ's robe where it overlaps pink drapery paint and the gilded background. Pure lead–tin yellow type II forms the surface paint. Reflected light, 327x. Photo: A. Roy.

speculate that the newer introduction (type I) may have been imported from Germany, accounting for an early name for the pigment, *giallo tedesco*.

In Bohemian painting, type II was identified on three paintings of the second half of the fourteenth century. Isolated occurrences were also reported by Kockaert (1984) in an altarpiece by Broederlam dated 1396, and in a Ter Brugghen dated 1627, in the National Gallery, London (no. 4164).

To complicate the question, it has been observed that in some samples of opaque bright yellow, particularly from certain schools of seventeenth-century Italian painting, spectrographic analyses show the presence of lead, tin, and antimony, while x-ray diffraction indicates a crystalline compound isostructural with lead-tin yellow II (cubic pyrochlore). It is unclear whether these yellows should properly be regarded as a modified variety of lead-tin yellow or as early examples of Naples yellow (lead antimonate). The d-values in the powder patterns suggest a pigment of intermediate composition. Some examples are cited by Bomford and Roy (1982). The stoichiometries and colors of compounds of this type have been studied by Ahmed (1962).

Relationship between Lead-Tin Yellow and Glass Manufacture

That the recipes to make "giallolino for painting" in the Bolognese manuscript are contained within a section relating to glass production may imply that a relationship existed between this pigment and the glass industry. Merrifield (1849) suggested, on the basis of this, along with statements

of Borghini (1584) and Baldinucci (1688), that one form of giallolino was made in Venice and composed of giallolino fino and giallo di vetro. Giallolino fino, she stated, is the yellow lead oxide we now call massicot, and giallo di vetro is the giallolino of the Bolognese manuscript. Of some relevance are the suggestions that the sections of the Bolognese manuscript relating to glass show Venetian connections as the source.

From studies of the incidence of lead-tin yellow, the occurrence of type II appears to have an association with (a) Florence in the fourteenth century and (b) with Venice and Bohemia in the sixteenth century (see Notable Occurrences). Bensi (1980) discussed the supply of pigments in Florence from the San Guisto Monastery in the fifteenth century, and noted that giallolino was one of those mentioned in documents. Colored glass was also apparently manufactured there. However, Antonio Neri's L'arte vetraria, published in Florence in 1612 contains no mention of glass-opacified yellow with a lead-tin oxide. Venice, on the other hand, was an important center for the production of colored enamel glass, and so the recipes contained in a manuscript by a Muranese glassmaker are particularly important (N. Eastaugh, private communication, 1986). Among these are yellows based on lead-tin oxide.

It is significant that in Lorenzo Lotto's "Account Book" of 1538-1542, in which supplies and prices of some of his painting materials are noted, there are apparently two kinds of lead-tin yellow which differ in price. One is described simply as zalolin (elsewhere as zallolino), and the other as zalolin da vazari (giallolino for vase makers, or lead-tin yellow for potters), the latter listed as costing twice the price of the former (see Zampetti, 1963). It is logical to identify the more expensive potter's yellow as lead-tin yellow type II, and zalolin as type I, especially since the early opacifiers for glass containing lead and tin have connections with ceramic glazes, which contain these components (see History of Use). The more involved method of the preparation of type II would account for its higher price.

Preparation

According to Jacobi (1941), lead-tin yellow I is obtained by heating in a crucible a mixture of about three parts of either lead monoxide, minium, or lead dioxide, with one part of tin dioxide, up to a temperature range of between 650° and 800°C. At 650°-700°C, warmer hues of yellow

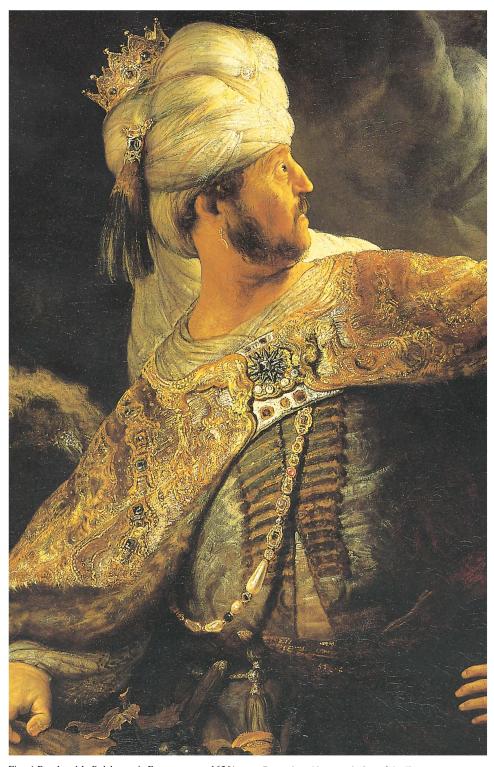


Fig. 4 Rembandt's *Belshazzar's Feast*, canvas, 1636/1638. National Gallery, London. No. 6350.

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A. Detail of the impasto on Belshazzar's cloak.



B. Cross section from a light yellow highlight on the embroidered cloak. The uppermost paint layer consists of lead–tin yellow type I and shows light-colored inclusions often seen in specimens of the pigment. These inclusions are usually either rich in tin, perhaps free stannic oxide, or show an excess of lead and silicon. The underlayers in the sample comprise a range of earth pigments over a double ground. Reflected light, 96x. Photo: A. Roy.

appear and at between about 720° and 800°C, the more lemon-colored hues similar to those on paintings develop (see fig. 8). The most beautiful hues are obtained with minium or lead dioxide. X-ray diffraction patterns of several samples obtained in this way at temperatures of between 650° and 800°C showed, as a main component, lead—tin oxide of the composition Pb₂SnO₄ (see X-ray Diffraction Data).

Lead-tin yellow I is also obtained without using silica following the procedure of recipe 273 of the Bolognese manuscript. It is possible that former methods of manufacture were based on metallic lead and tin. Furthermore, it is believed that lead-tin yellow I obtained without silica is identical to the *giallolino fino* mentioned by Merrifield (1849), which is said to have originated in Flanders.

Lead-tin yellow II is obtained according to recipe 273 as a yellow lead glass that begins to melt at 500°C. At temperatures of 900°-950°C an intense yellow glass mass forms, which, when pulverized, shows the lemon-yellow hue of lead-tin yellow I obtained at 720°-800°C.

The preparation of lead–tin yellow II according to recipe 273 of the Bolognese manuscript is similar to the preparation of a cubic lead–tin oxide, PbSnO₃, Pb(Sn,Si)O₃, or PbSn₂SiO₇ (see also Composition), described by Rooksby (1964): "pre-formed Pb₂SnO₄ is doped with silica and heated up to a temperature range of 800°–950°C."

It may be assumed that the lead—tin yellow II obtained according to recipe 273 is identical with giallo di vetro (yellow from glass) mentioned by Merrifield (1849), which is said to have come from Venice. While recipe 272 does not produce a glass melt which could be used for manufacturing rosary beads, it is possible that the melt obtained according to recipe 273 was used for this purpose. Our investigations suggest that recipe 272 was only used as a first step to recipe 273 (Kühn, 1967).

Particle Characteristics

Under the optical microscope, lead-tin yellow I and II show hardly any definitive characteristics; both types consist of fine particles, sometimes with a sharp-edged conchoidal fracture (fig. 5A–C), although in certain specimens identified as type II, rather larger lemon-yellow crystalline particles may be present.

At high magnifications in the scanning electron microscope, reference specimens of types I and II show distinctive particle morphology (see fig. 6A and B.)

Optical Properties

Microscopically, lead-tin yellow I and II are seen by transmitted light to consist of yellow highly refracting particles of vitreous appearance. The refractive index of both types is higher than 2.0 and corresponds to about that of Naples yellow. Gmelins Handbuch gives refractive indices for Pb₂SnO₄ as $\omega = 2.29$, $\varepsilon = 2.31$ (Gmelins Handbuch, 1971). Due to their high refractive index, lead-tin yellow I and II show strong relief in media with a low refractive index (Canada balsam, Aroclor, and so on). According to the JCPDS Data File, lead-tin yellow I belongs to the tetragonal system. Lead-tin yellow II has a cubic pyrochlore-type crystal structure and accordingly, is isotropic. Lead-tin yellow I is birefracting, but because of the intense color of the particles, the characteristic interference colors cannot be observed.

Chemical Properties

Lead-tin yellow I and II are little affected by dilute HCl, HNO₃, and H₂SO₄ in the cold. Even on boiling with concentrated acids, decomposition is slow. Both types of the yellow are unaffected by alkalis and can, therefore, be used in lime medium. Hydrogen sulfide or soluble sulfides cause

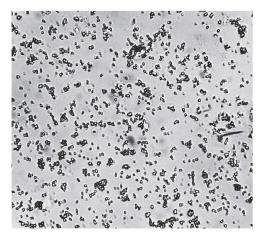
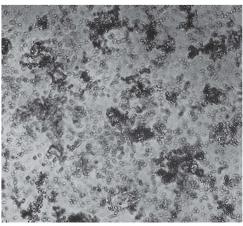
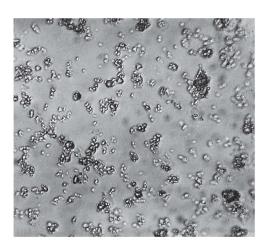


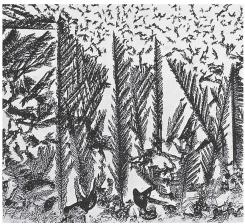
Fig. 5 A. Particles of lead–tin yellow from a specimen of paint from an oil painting attributed to Albert Bouts, Assumption of the Virgin. After treatment of a tiny paint sample and dispersion of the particles with 5% KOH, the residue was washed with water, dried, and then mounted in methylene iodide, n = 1.74. Photomicrograph c.450x; bright field with cover glass.



C. Specimen of lead–tin yellow from a mural painting in the Collegial Church, Nivelles, Belgium, probably fourteenth century (specimen E2/107 Institut Royal du Patrimoine Artistique, Brussels), mounted in methylene iodide, n = 1.74. Photomicrograph c. 473x. bright field with cover glass.



B. Same preparation, c. 722x.

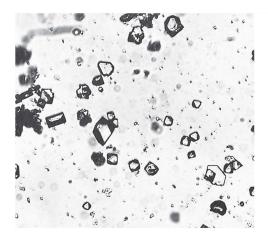


D. The feathery crystals of the mixed chlorides of lead and tin were formed from the Nivelles sample after treatment with aqua regia and concentrated HCl. Photomicrograph c. 74x, bright field, dry preparation without cover glass.

blackening with formation of lead sulfide. Prolonged heating of lead-tin yellow I and II to temperatures of about 900°C causes decomposition, as indicated by an increased amount of free tin oxide.

General Pigment Properties

Both types of lead—tin yellow are heavy yellow powders. Due to their relatively high refractive index when used in oil- and in oleo—resinous media, they have high hiding power, similar to Naples yellow. The oil absorption is between 15% and 25% by weight.



E. Same preparation as D. Test for tin with RbCl to form tiny octahedra of Rb₂SnCl₆; after procedure described on p. 94. Photomicrograph 236x, bright field, in aqueous solution without cover glass.

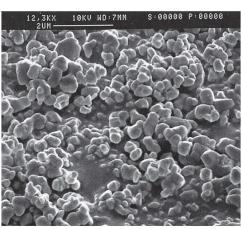
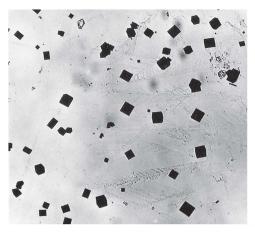
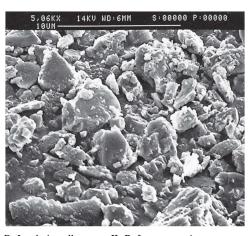


Fig. 6 Scanning electron micrographs of lead–tin yellow.

A. Lead-tin yellow type I. Reference specimen prepared at the National Gallery, London; identity confirmed by XRD (see fig. 7A). Gold-coated, printed at 7,872x.



F. Test for lead with triple nitrite reagent according to the procedure described on p. 94. Photomicrograph 95x, bright field, test solution without cover glass.



B. Lead-tin yellow type II. Reference specimen prepared at the National Gallery, London; identity confirmed by XRD (see fig. 7D). Gold-coated, printed at 3,238x. Photos: A. Roy.

In oil-media (linseed oil, poppy oil, and so on) lead—tin yellow I and II accelerate drying in the same way as lead white and other lead compounds. Just as in the case of lead white, fatty acid lead salts are formed during the drying process. These can be detected on paintings and in aged samples by means of infrared absorption spectrometry.

Permanence and Compatibility with Other Pigments and Media

Lead-tin yellow I and II—in contrast to yellow lead oxide (PbO) which darkens readily, especially in aqueous media—are not affected by light (Denninger, 1955). Lead-tin yellow I and II in media such as linseed oil, poppy seed oil, egg tempera, casein, and plant gum have been tested at the Doerner Institute under a xenon-lamp, a mercury vapor lamp, and in daylight. The lack of

reaction to light may also be a reason for the use of lead-tin yellow in place of lead monoxide. On paintings, lead-tin yellow I has been found mixed with lead white (basic lead carbonate), with vermilion, ochre, yellow lakes, verdigris (basic and neutral copper acetates), and with azurite and indigo. Most frequent among them are mixtures with verdigris, azurite, and white lead-combinations commonly found for the bright green underpaints in the foliage and landscapes of Early Netherlandish School paintings, often in conjunction with a surface glaze of "copper resinate" (see chapter 6). On none of the paintings examined so far, has a change been noted. This is also true of artificially aged samples of lead-tin yellow I and II mixed with the above-mentioned pigments in oil-medium.

Lead-tin yellow has been identified on European easel paintings in oil-, oil-resin, and tempera media, as well as in mural paintings in contact with lime. No suggestion of alteration has been found in any of these cases. In oil-, oil-resin, or tempera media, reaction with other pigments and with airborne impurities is largely excluded. In pure aqueous media, for example in gum arabic, the possibility of formation of black lead sulfide exists.

Microchemical Tests

Although lead and tin can be detected by microchemical tests, it is not possible to distinguish between types I and II by this means (see X-ray Diffraction Analysis).

Test for Tin with Rubidium Chloride to Form Rb₂SnCl₆

A tiny sample (0.1-0.5 mm diameter) is treated in a cupped microscope slide with a small drop (2–3 mm diameter) of concentrated HNO₃ to precipitate the tin as white metastannic acid. After it evaporates to dryness, the residue is taken up with aqua regia (1 drop concentrated HNO₃ plus 2 drops concentrated HCl), heated to dryness, and the operation is repeated three times. The residue is soluble only with difficulty, hence to complete the reaction, it is often necessary to make a final treatment with aqua regia plus 1 drop of concentrated HCl and let it stand. On slow evaporation, feathery crystals of mixed lead and tin chlorides form (see fig. 5D). This residue is next taken up in a medium-sized drop of 50% HCl. By means of a dropping rod, a small drop is lifted from the upper portion of the solution drop and transferred to a flat slide. Two or three grains of RbCl are then

added. If tin is present, a cloud of tiny crystals (octrahedra) of Rb₂SnCl₆ soon appears. On slow evaporation in the air, the crystals may grow in size (see fig. 5E; also Geilmann, 1954; pl. 24, no. 5).

Test for Lead with Potassium Iodide to Form PbI₂

A paint sample of a few micrograms is warmed with a drop of nitric acid and heated to dryness. By repeating this process several times, a sufficient amount of lead from the lead–tin yellow becomes soluble as nitrate, so that it may be identified as lead iodide. For this purpose, the residue is taken up with dilute acetic acid, gently warmed, and a grain of potassium iodide added. In the presence of lead, lead iodide is deposited and is in the form of yellow iridescent six-sided laminae (Geilmann, 1954; pl. 42, no. 3; see also chapter 3, figs. 14 and 15).

Alternative Test for Lead with Triple Nitrite to Form K₂CuPb(NO₂)₆

Another drop of the same preparation is evaporated to dryness on another slide. The residue is covered with a drop of triple nitrite reagent (0.9 g Cu(Ac)₂; 2 g KNO₂; 0.2 ml HAc; 15 ml H₂O). If Pb²⁺ ions are present, they precipitate as tiny dark brown cubes of K₂CuPb(NO₂)₆ from a greenish solution (fig. 5F).

Criteria for Certain Identifiction

Microscopic identification is uncertain since lead—tin yellow particles, especially in mixtures with other pigments, show few marked characteristics. For positive identification, the presence of lead and tin must be shown. No other yellow pigment contains tin as an essential constituent, so that a high tin content is to be regarded as characteristic for lead—tin yellow, although considering the comments under Relative Frequency of Use, the absence of antimony should perhaps also be established. Mosaic gold (tin disulfide, SnS₂) is sufficiently distinctive under the microscope for confusion not to arise.

Although lead-tin yellow II contains additional silicon, the presence of silicon (Si) is not a distinct criterion for lead-tin yellow II, because silicon may also be present in other pigments (for instance, earth pigments) and in some cases, samples of lead-tin yellow I. Distinction between lead-tin yellow I and II, according to our experience, is best achieved by x-ray diffraction analysis.

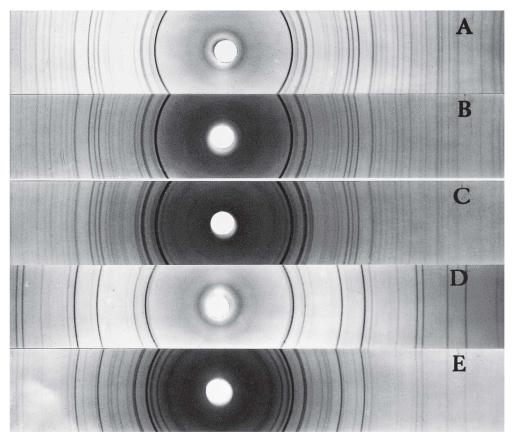


Fig. 7 X-ray powder diffraction patterns for lead-tin vellow.

- A. Lead-tin yellow type I, reference standard, National Gallery, London.
- B. Lead-tin yellow type I, from the yellow candle flame in Rubens' *Samson and Delilah*. National Gallery, London, No. 6461.
- C. Lead-tin yellow type I, from a foliage highlight in Titian's *The Death of Actaeon*. National Gallery, London, No. 6420.
- D. Lead-tin yellow type II, reference standard, National Gallery, London.
- E. Lead-tin yellow type II, from the background of *The Pentecost*, ascribed to Giotto. National Gallery, London, No. 5360. The specimen also contains a little lead white.
- Photographs not to be used for measurement purposes. XRD patterns by A. Roy.

Emission Spectrometric Analysis

This method is preferred at the Doerner Institute. For qualitative analysis a few micrograms of paint are sufficient. In comparison with microchemical methods, spectrometric analysis has an advantage—with one single spectrogram other elements can be detected simultaneously and the absence of certain elements can be proven as well. Characteristic lines for lead are at 4057.8, 3683.5, 3639.6, 2873.3, 2833.1, 2802.0, and 2614.2 Å; for tin they are at 3262.5, 3175.0, 2863.3, and 2840.0 Å.

X-ray Diffraction Analysis

This method allows the differentiation between lead—tin yellow I and II. X-ray diffraction patterns may be taken with a Debye-Scherrer camera, using a few micrograms of substance fixed on a glass thread (see fig. 7). The same sample may subsequently be used for emission spectrometric analysis.

The most characteristic lines for the detection of lead–tin yellow I and II are given in table 1. Fuller data are presented in tables 2 and 3.

The d-values of lead-tin yellow I identified on

Table 1 Characteristic Lines for Detection of Lead-Tin Yellow I and II

Yellow II	Lead Tin Y	Lead Tin Yellow I	
1	d (Å)	I	d (Å)
100	3.081	100	3.350
60	2.660	40	3.098
70	1.891	65	2.770
70	1.612	70	1.858
20	1.541	70	1.803
		80	1.726
		65	1.574

The combination of the three lines in brackets is also typical.

paintings and the d-values of samples prepared in the laboratory on the whole agree with those listed in the JCPDS Data File (nos. 3–1122 and 11–233) for the compound Pb₂SnO₄. Besides these lines, there are often other lines attributable to SnO₂. Intensity variations are probably due to different measuring methods.

A more recent pattern for Pb₂SnO₄ has been reported to the JCPDS Data File (no. 24-589) giving the eight strongest d-values as: 3.32 [100], 2.76 [30], 2.81 [20], 1.72 [20], 1.85 [20], 2.56 [10], 1.80 [10], and 1.57 [10]. (Relative intensities in brackets.)

Of the five paintings marked with D* in the list of Notable Occurrences, a second type of lead-tin oxide that contains additional silicon has been found. The x-ray diffraction patterns of these yellow color samples agree satisfactorily among themselves with regard to the most significant lines, designated by c. These lines are also the dominant lines in lead-tin yellow samples prepared in our laboratory (Doerner Institute) and in Rooksby's (1964) compound. The x-ray diffraction pattern of lead-tin II, in similarity to type I, shows additional lines for free SnO₂.

X-ray Fluorescence Analysis and **Electron Micro-beam Probe Analysis**

By x-ray fluorescence analysis it might be possible to detect lead (Pb) and tin (Sn) in situ on a picture without taking a sample.

The main lines for lead are $K\alpha_1 = 75.0$ keV, $K\alpha_2 = 72.8 \text{ keV}, L\alpha_1 = 10.6 \text{ keV}, \text{ and } L\beta_2 = 12.6$ keV; for tin they are: $K\alpha_1 = 25.3$ keV, $K\alpha_2 = 25.0$ keV, $K\beta_1 = 28.5$ keV, and $K\beta_3 = 28.4$ keV.

Lead-tin yellow in areas of yellow and mixed green paint has been detected using x-ray fluores-

Table 2 X-ray Diffraction Data for Lead-Tin Yellow I

SnPb JCPDS No. 3-	File	Lead- Yellow Painting Samp Prepared Doerner	I from gs and oles d at the	Pb ₂ S JCPD No. 11	S File
<u>d</u> (Å)	I	d(Å)a	I ^b	d(Å)	I
3.32	28	3.350	100^{c}	3.30	100
3.15	4 4	2 000	40°	2.06	40
3.08 2.82	4	3.098	40°	3.06	40
				2.79	60
2.77	8	2.770	65°	2.75	80
2.55	4	2.555	15	2.54	60
2.26	4	2.252	20	2.25	40
2 10	4	2 170	20	2.20	20
2.18 2.07	4 4	2.179	20	2.17 2.07	40 20
2.07	4			2.07	20
2.02	12	2.013	50	2.00	60
1.95	8	1.948	35	1.95	60
1.89	4	1.740	33	1.91	20
1.85	50	1.858	70°	1.71	20
1.80	32	1.803	70°		
1.77	4	1.005	, 0		
1.73	100	1.726	80c		
1.69	4				
1.61	8				
1.57	50	1.574	65°		
1.54	28	1.545	25		
1.51	4				
1.49	8	1.495	25		
1.47	4	1.474	30		
1.46	8	1.416	20		
1 40	4	1.416	20		
1.40 1.37	4				
1.37	24 24				
1.33	16				
1.20	10				
1.22	8				
1.20	8				
1.14	12				
1 12	12				
1.13 1.12	4				
1.12	8				
1.07	4				
0.945	4				
0.934	8				
0.824	4				
J.U2T	7				

JCPDS data courtesy of JCPDS International Centre for Diffraction Data.

a. In addition to the lines listed here, others at 2.642, 2.367,

^{1.764,} and 1.674 Å may be attributed to SnO₂.

b. Intensities measured photometrically on the x-ray powder

c. Characteristic lines for lead-tin yellow I. The combination of the three lines bracketed together is also typical.

Table 3 X-ray Diffraction Data for Lead-Tin Yellow II

		Sample			
		Yell			
		Backgro			
		the Peni Ascrib			
		Gio			
San	nple	(Natio			
	red at	Galle		Сотрои	nd
	rner	Lond		Prepared	
Inst	itute	No.53	360)	Rooksby (1	964)
d(Å)	I ^a	d(Å)	I ^b	d(Å)	I
6.14	10	6.15	10	6.17	15
3.325	30	3.26	10	3.223	10
3.081	100c	3.09	100	3.087	100
2.660	60^{c}	2.67	50	2.673	60
0.447	10	2.45	10	0.450	10
2.447 2.367	10 10 ^d	2.45	10	2.453	10
1.891	70°	1.89	70	1.890	70
1.071	70	1.81	5	1.807	5
		1.01	5	1.007	2
1.758	50^{d}				
1.668	10^{d}				
		1.635	5	1.631	2
1.612	70°	1.615	70	1.611	65
1.541	20°	1.542	10	1.543	15
1.496	10	1.490	5	1.497	2
1.438	15 ^d				
1.412	15 ^d	1 202	_	1 202	2
1 240	1.5	1.392	5	1.392	3
1.340 1.324	15 15 ^d	1.336	10	1.336	8
1.224	30	1.226	20	1.226	20
1.216	30⁴ 10⁴	1.220	20	1.220	20
1.193	30	1.195	20	1.195	15
1.156	5ª	1.175	20	1.175	13
		1.175	5	1.174	1
1.090	20	1.091	10	1.091	10
1.080	10^{d}				
		1.029	10	1.029	15
				0.9454	3
				0.9038	10
				0.8910	7
				0.8452	5
				0.8156	4
				0.8057	4
				0.0037	

a. Intensities measured photometrically on the x-ray powder patterns.

cence (XRF) surface analysis in a number of paintings in the collection of the National Gallery of Art, Washington. Examples include: the light-green foreground and highlights on foliage in Giovanni Bellini's *The Feast of the Gods* (Widener Collection, no. 1942.9.1); the foliage of Dosso Dossi's *Circe and Her Circle of Lovers* (no. 1943.4.49); the green sleeves of Raphael's *Niccollini-Cowper Madonna* (no. 1937.1.25); and in yellow highlights on Rembrandt's *A Polish Nobleman* (no. 1937.1.78). Both lead and tin were found at concentrations that suggest the use of the yellow pigment. In order to detect tin, a BaCl₂ secondary target is used (Barbara H. Berrie, private communication).

Electron micro-beam probe analysis may be used to detect lead and tin in specimens from pictures.

Visual, Infrared, and UltravioletSpectrophotometry

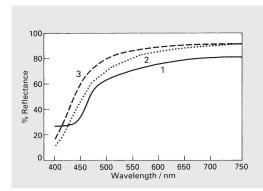
Identification of lead-tin yellow I and II with the aid of infrared spectrometry is only possible in the long wavelength portion of the spectrum since neither variety has bands within the range of 2000-600 cm⁻¹. Vigouroux et al. (1982) recorded vibrational spectra below 600 cm⁻¹ for lead-tin yellow I, with bands at 573, 495, 451, 421, 364, and 320 cm⁻¹ in the infrared, and at 540, 457, 379, 292, 275, 196, 129, 80, and 35 cm⁻¹ in the Raman spectrum. Wainwright et al. (1986) published the far infrared spectra of both forms and showed that lead-tin yellow type II yields absorptions at about 460, 430, and 305 cm⁻¹, with possibly some further bands below 300 cm⁻¹. The results suggest that the two structures may be distinguished by infrared spectroscopy.

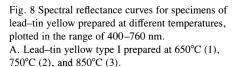
In ordinary white light both types of lead-tin yellow are usually canary in hue. Color reflectance curves for samples of lead-tin yellow I and II prepared at a range of temperatures are shown in figure 8A and B. The samples differ little in their hues—lead-tin yellow II having a very slight greenish tone in comparison with lead-tin yellow I. As already mentioned, the hue of each variety of yellow depends to a large extent on the manufacturing temperature. Preliminary studies by Nicholas Eastaugh (private communication) have indicated that trace or minor constituents in lead-tin yellow, such as copper and manganese, also play a significant role in determining the final color of the product.

b. Intensities visually estimated.

c. Lines found in all samples from paintings.

d. Attributable to SnO2.

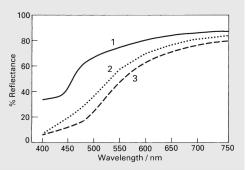




Within the ultraviolet range of 190–350 nm, the reflectance values for lead–tin yellow I and II are between 3.5% and 7%, depending on the wavelength. The reflectance values within the near-infrared range of 760–1,000 nm are, to a large extent, independent of the wavelength and lie between 80% and 95%.

X-radiography

Lead—tin yellow on paintings, like lead white, Naples yellow, and vermilion, shows high absorption coefficients for x-rays; therefore, the lead—tin yellow parts on paintings appear on x-ray negatives as relatively light areas (that is, the pigment is opaque to x-rays). Rees Jones (1975) gave lead—



B. Lead-tin yellow type II prepared at 650°C (1), 750°C (2), and 850°C (3). Specimen preparation and color measurement by N. Eastaugh. Curves courtesy of D. Saunders.

tin yellow I as the most x-ray absorbing of artists' pigments, greater even than lead white.

Notable Occurrences

Besides the occurrences of lead-tin yellow mentioned in the literature under History of Use, the Doerner Institute has identified the presence of lead-tin yellow in 158 other works of art. This identification was carried out with the aid of emission spectrometric analysis, in thirty-four cases supplemented by x-ray diffraction analysis (marked with D or D* in the list). In addition, there are listed occurrences observed in other laboratories.

Notable Occurrences

I. Lead-tin yellow identified by H. Kühn.

Identification by emission spectrometric analysis, and in some cases $(D,\,D^*)$ by x-ray diffraction pattern. D indicates lead-tin yellow I; D* lead-tin yellow II.

Date	Artist and Title	Gallery, Inventory No.	
Easel Paintings c.1300	Giotto The Last Supper	BSTG, Inv.No.643	
c.1350	Nardo di Cione Five Saints	BSTG, Inv.No.waf 1027	
2nd third 14th C	D* Master of the Hohenfurther Passion Cycle Passion Cycle	Nârodni Gallery, Prague	
2nd half 14th C	Taddeo Gaddi St. Francis Offers before the Sultan to Undergo the Test of Fire	BSTG, Inv.No.10677	
4th quarter 14th C	D* Master of the Wittingauer Altar Wittingauer Altar	Nârodni Gallery, Prague	
4th quarter 14th C	D* Master of the Wittingauer Altar, Workshop Martyrdom of St. Barbara	Nârodni Gallery, Prague	
end 14th C	D Bohemian The Annunciation	Institut für Denkmalpflege (Institute for the Care of Monuments, Dresden)	
c.1420	Masolino da Panicale Madonna and Child	bstg Inv.No.waf 264	
c.1440	Fra Angelico The Saints before the Judge	BSTG, Inv.No.waf 37	
c.1440	Fra Angelico The Martyrdom of Sts. Cosmas and Damian	BSTG, Inv.No.WAF 38	
1st half 15th C	Master of the Bambino Vispo The Last Judgment	BSTG, Inv.No.10201	
2nd quarter 15th C	Giovanni di Paolo Two Scenes from the Legend of St. John	BSTG, Inv.No.L884, L885	
c.1450	German The Adoration of the Kings	Private collection, Munich	
c.1455	Fra Filippo Lippi Virgin and Child	BSTG, Inv.No.647	
c.1460	Rogier van der Weyden The St. Columba Altarpiece (see fig. 1)	BSTG, Inv.No.WAF 1189	
c.1470	D Dieric Bouts the Elder The Resurrection of Christ	BSTG, Inv.No.neu 1449	
1481–1487	D Hinrik van dem Kroghe Altarpiece	Ratzeburg Cathedral	

Date	Artist and Title	Gallery, Inventory No.
c.1483	Michael Pacher Altar of the Church Fathers	BSTG, Inv.No.2597-2600
4th quarter 15th C	D Michael Pacher The St. Lawrence Altar	BSTG, Inv.No.2592, 5304-5306
4th quarter 15th C	Piero di Cosimo Scene from the Story of Prometheus	BSTG, Inv.No.8973
c.1500	Baldassare Estense(?) Family Group	BSTG, Inv.No.8709
c.1500	Cima da Conegliano The Virgin and Child with St. Mary Magdalene and St. Jerome	BSTG, Inv.No.992
c.1500	Netherlandish Landscape	BSTG, Inv.No.9893
c.1500	Nurembergish The Sending Out of the Apostles	BSTG, Inv.No.1494
1st quarter 16th C	Franciabigio Madonna and Child	BSTG, Inv.No.8886
1st quarter 16th C	Matthias Grünewald The Blessed Erasmus and St. Mauritius	BSTG, Inv.No.1044
1st quarter 16th C	Sodoma (Giovanni Antonio Bazzi) The Holy Family	BSTG, Inv.No.waf 1025
c.1520–1530	Giovanni Antonio Sogliani Virgin and Christ Child with St. John the Baptist	Danish Royal Family
1526	Albrecht Dürer Apostles	BSTG, Inv.No.540, 545
c.1536	Jan van Hemessen (Jan Sanders) Isaac Blessing Jacob	BSTG, Inv.No.10
c.1540	Giorgio Vasari Holy Family with Infant John	BSTG, Inv.No.waf 1150
1542	Marinus van Roymerswaele A Notary	BSTG, Inv.No.718
2nd quarter 16th C	Albrecht Altdorfer The Alexander Battle	BSTG, Inv.No.688
2nd quarter 16th C	Bartholomäus Bruyn the Elder The Virgin and Child	BSTG, Inv.No.waf 155
1572	Lucas Cranach the Younger The Elector Augustus and His Family before the Crucifix	Chapel of the Castle of Augustusburg, Erzgebirge, Altarpiece
c.1595	Gillis van Coninxloo(?) Forest Landscape with Hagar and Ishmael	BSTG, Inv.No.6328
2nd half 16th C	Giulio Cesare Procaccini The Virgin, Child, and the Young John the Baptist	BSTG, Inv.No.450
c.1515	Titian The Vanity of Earthly Things	BSTG, Inv.No.483

Date	Artist and Title	Gallery, Inventory No.
1542	D Titian A Venetian Nobleman	BSTG, Inv.No.waf 1085
1548	D Titian Portrait of the Emperor Charles V	BSTG, Inv.No.632
c.1560	D Titian The Virgin and Child in an Evening Landscape	BSTG, Inv.No.464
3rd quarter 16th C	Titian Christ Crowned with Thorns	BSTG, Inv.No.2272
2nd quarter 16th C	Tintoretto Mars and Venus Surprised by Vulcan	BSTG, Inv.No.9257
1570/1580	Tintoretto Christ in the House of Martha and Mary	BSTG, Inv.No.4788
before 1579	D* Tintoretto Gonzaga Cycle. 1st Row: The Emperor Creating Gianfranco Gonzaga First Marquis of Mantua	BSTG, Inv.No.7303
before 1579	D* Tintoretto Gonzaga Cycle. 1st Row: The Battle of Legnano	BSTG, Inv.No.7304
before 1579	Tintoretto Gonzaga Cycle. 1st Row: The Relief of Legnano	BSTG, Inv.No.7307
before 1579	Tintoretto Gonzaga Cycle. 1st Row: The Battle on the Taro	BSTG, Inv.No.7309
1579/1580	D Tintoretto Gonzaga Cycle. 2nd Row: 1. <i>The Capture of Milan</i>	BSTG, Inv.No.7305
1579/1580	D TintorettoGonzaga Cycle. 2nd Row:2. The Capture of Parma	BSTG, Inv.No.7306
1579/1580	Tintoretto Gonzaga Cycle. 2nd Row: 3. <i>The Capture of Pavia</i>	BSTG, Inv.No.7308
1579/1580	Tintoretto Gonzaga Cycle. 2nd Row 4. Entry of Philip II into Mantua	BSTG, Inv.No.7302
1609	D Peter Paul Rubens Rubens and Isabella Brant in a Honeysuckle Bower	BSTG, Inv.No.334
c.1610	D Peter Paul Rubens The Dying Seneca	BSTG, Inv.No.305
1615/1616	Peter Paul Rubens Martyrdom of St. Lawrence	BSTG, Inv.No.338
c.1616	Peter Paul Rubens The large Last Judgment	BSTG, Inv.No.890

Date	Artist and Title	Gallery, Inventory No.
1616/1617	Peter Paul Rubens The Rape of the Daughters of Leukippos	BSTG, Inv.No.321
c.1620	D Peter Paul Rubens The Fall of the Damned	BSTG, Inv.No.320
1622	D Peter Paul Rubens The Fall of the Angels	BSTG, Inv.No.306
1st quarter 17th C	Peter Paul Rubens Hippopotamus Hunt	BSTG, Inv.No.4797
1st quarter 17th C	Peter Paul Rubens Lion Hunt	BSTG, Inv.No.602
c.1624/1625	D Peter Paul Rubens The Apocalyptic Woman	BSTG, Inv.No.891
c.1635	Peter Paul Rubens Meleager and Atalanta	BSTG, Inv.No.355
c.1635	D Peter Paul Rubens The Massacre of the Innocents	BSTG, Inv.No.572
c.1636/1640	D Peter Paul Rubens Susanna and the Elders	BSTG, Inv.No.317
1627	Rembrandt St. Paul in Prison	Staatsgalerie Stuttgart Inv.No.746
1633	Rembrandt Bust Portrait of a Man in Turkish Dress	BSTG, Inv.No.421
1636	Rembrandt The Ascension	BSTG, Inv.No.398
1639	Rembrandt The Resurrection	BSTG, Inv.No.397
1646	Rembrandt The Adoration of the Shepherds	BSTG, Inv.No.393
c.1650	Rembrandt Flora	Metropolitan Museum, New York, Inv.No.26.101.10
1655	Rembrandt Joseph and Potiphar's Wife	Staatliche Museen, Berlin Cat.No.828H
c.1655	Jan Vermeer Diana and Her Companions	Mauritshuis, The Hague Inv.No.406
1656	D Jan Vermeer The Procuress	Gemäldegalerie, Dresden Inv.No.1335
c.1656	Jan Vermeer Girl Asleep	Metropolitan Museum, New York, Inv.No.14.40.611
c.1657	Jan Vermeer The Soldier and the Laughing Girl	Frick Collection, New York Inv.No.A936
c.1658	D Jan Vermeer Girl Reading a Letter at an Open Window	Gemäldegalerie, Dresden Inv.No.1336
c.1660	Jan Vermeer Maidservant with a Milk Pitcher	Rijksmuseum, Amsterdam Inv.No.2527 A1
c.1661	Jan Vermeer Gentleman and Lady Drinking Wine	Staatliche Museen, Berlin Inv.No.912C

Date	Artist and Title	Gallery, Inventory No.
c.1663	D Jan Vermeer The Girl with the Wine Glass	Herzog-Anton-Ulrich Museum Brunswick, Inv.No.316
c.1670	D Jan Vermeer Mistress and Maidservant	Frick Collection, New York Inv.No.A1002
c.1600	D Hendrik Goltzius Sketchbook Leaf with Sheep and Camels	Staatliche Graphische Sammlung, Munich Inv.No.12196/97
1607	Abraham Janssens van Nuyssen The Raising of Lazarus	BSTG, Inv.No.153
c.1610	Abraham Janssens van Nuyssen Diana and Her Nymphs	BSTG, Inv.No.13111
2nd decade 17th C	D Abraham Janssens van Nuyssen Mount Olympus	BSTG, Inv.No.4884
1611	Elias Greuter Massacre of the Innocents	BSTG, Inv.No.1435
c.1615	D Pieter Candid The Fishery	BSTG, Inv.No.4219
1624	Pieter Candid The Holy Ghost	BSTG, Inv.No.2687
1624	D Pieter Candid The Blessed Carl Borromäus	BSTG, Inv.No.1917
1620	Pieter Lastman The Baptism of the Moorish Chamberlain	BSTG, Inv.No.10735
1622	D Johann Rottenhammer The Virgin with Sts. John the Baptist and Anthony of Padua	BSTG, Inv.No.4575
c.1622	Anthony van Dyck Self-Portrait	BSTG, Inv.No.405
1623	Gerard van Honthorst The Prodigal Son	BSTG, Inv.No.1312
c.1624	Cornelis de Vos Portrait of a Man	BSTG, Inv.No.6306
c.1624	Cornelis de Vos Portrait of a Woman	BSTG, Inv.No.6303
1st quarter 17th C	Johann von Aach Hausser Ecce Homo	BSTG, Inv.No.6421
1st quarter 17th C	Alexander Keirincx Wooded Landscape with the Rest on the Flight into Egypt	BSTG, Inv.No.6304
1st quarter 17th C	Joos de Momper Mountain Landscape	BSTG, Inv.No.6430
1st quarter 17th C	Joos de Momper Mountain Landscape	BSTG, Inv.No.6536
1st quarter 17th C	Carlo Saraceni The Death of the Virgin	BSTG, Inv.No.185
1st quarter 17th C	Sebastian Vrancx Sudden Attack	BSTG, Inv.No.6295

Date	Artist and Title	Gallery, Inventory No.
1st half 17th C	Sebastian Vrancx Busy Street Scene in a Flemish Town	BSTG, Inv.No.5690
1st quarter 17th C	Frans Francken the Younger The Fall Under the Cross	BSTG, Inv.No.6279
2nd quarter 17th C	Frans Francken the Younger Virtue and Vice	BSTG, Inv.No.860
c.1630	Abraham Bloemaert John the Baptist Preaching	BSTG, Inv.No.2045
c.1630	D Nicolas Poussin The Lamentation	BSTG, Inv.No.625
1634	Bonaventura Peeters Sailing Boats before a Town	BSTG, Inv.No.6332
c.1635	Jacob van Moscher Village Party in Zealand	BSTG, Inv.No.3075
1639	Salomon van Ruisdael River Scene with Ferry	BSTG, Inv.No.161
3rd quarter 17th C	Salomon van Ruisdael Canal Landscape with Castle Nijenrode	BSTG, Inv.No.6497
c.1640	Aelbert Cuyp Landscape, Flat Country	BSTG, Inv.No.1214
c.1640	Johann Heinrich Schönfeld The Defeat of Pyrrhus	BSTG, Inv.No.9774
c.1645	Ferdinand Bol Self-Portrait	BSTG, Inv.No.609
c.1660	Ferdinand Bol The President of the Vintners' Guild	BSTG, Inv.No.9656
1647	Jacob van Ruisdael Sandhill with Trees	BSTG, Inv.No.1022
1649	Guillaume Dubois Village Landscape	BSTG, Inv.No.6379
2nd quarter 17th C	Adriaen Brouwer Peasants Smoking and Drinking in a Tavern	BSTG, Inv.No.2062
2nd quarter 17th C	Adriaen Brouwer The Sleeping Inn-keeper	BSTG, Inv.No.2014
2nd quarter 17th C	Adriaen Brouwer Peasant Quartet	BSTG, Inv.No.109
2nd quarter 17th C	Pietro da Cortona Rest on the Flight to Egypt	BSTG, Inv.No.176
2nd quarter 17th C	Georg Flegel Meal Table with Fried Eggs	BSTG, Inv.No.5025
2nd-3rd quarter 17th C	Willem Romeyn Herd of Cattle	BSTG, Inv.No.9486
2nd-3rd quarter 17th C	Daniel Seghers The Holy Family Surrounded by a Garland	BSTG, Inv.No.6305

Date	Artist and Title	Gallery, Inventory No.
1650	Jan Fyt Dead Game Guarded by Dogs	BSTG, Inv.No.805
1653	Abraham van Beyeren Large Still Life with Lobster	BSTG, Inv.No.1620
1654	Gerard Dou An Old Woman Selling Vegetables and Herrings	BSTG, Inv.No.552
c.1657	Pieter Neeffs the Younger Interior of a Gothic Church	BSTG, Inv.No.6473
c.1660	Karel du Jardin The Sick Goat	BSTG, Inv.No.291
1664	Jan van Kessel Rome from the Europe Cycle	BSTG, Inv.No.1910
1664	Jan Steen Fight between Card-players in an Inn	BSTG, Inv.No.276
1668	José Antolinez Maria Immaculata	BSTG, Inv.No.7716
3rd quarter 17th C	Jan Davidz. de Heem Still Life of Flowers with a Skull	BSTG, Inv.No.568
3rd quarter 17th C	Abraham Mignon Fruit	BSTG, Inv.No.6427
3rd quarter 17th C	Klaes Molenaer Skating Scene	BSTG, Inv.No.6457
3rd quarter 17th C	Hendrik Mommers Roman Market	BSTG, Inv.No.6396
3rd quarter 17th C	Aert van der Neer Sunset	BSTG, Inv.No.6381
3rd quarter 17th C	David Teniers the Younger Repast with Monkeys in Costume	BSTG, Inv.No.816
3rd quarter 17th C	Caspar de Witte <i>Mountain Landscape</i>	BSTG, Inv.No.6297
3rd quarter 17th C	Philips Wouwerman Horses at the Water	BSTG, Inv.No.880
1680	Caspar Netscher Young Cavalier	BSTG, Inv.No.6323
2nd half 17th C	Frans de Hamilton(?) Still Life with Birdsnest and Grasshopper	BSTG, Inv.No.6531
2nd half 17th C	Willem de Heusch Landscape with Sunset	BSTG, Inv.No.6442
2nd half 17th C	Pieter Wouwerman Soldiers Playing Dice in Front of an Inn	BSTG, Inv.No.6403
1684	Aert de Gelder The Jewish Bride	BSTG, Inv.No.841
c.1715	Aert de Gelder Noli me Tangere	BSTG, Inv.No.6318

Date	Artist and Title	Gallery, Inventory No.
1702	Eglon Hendrik van der Neer Mountain Landscape	BSTG, Inv.No.5239
1721	Jan Joost van Cossiau Landscape with the Wise and the Foolish Virgins	BSTG, Inv.No.6508
1723	Jan Joost van Cossiau Midday	BSTG, Inv.No.6524
1728	Jan Joost van Cossiau Afternoon	BSTG, Inv.No.6494
1st quarter 18th C	Sebastiano Ricci The Temptation of St. Anthony	BSTG, Inv.No.2263
2nd quarter 18th C	Canaletto The Piazetta and the Riva de Schiavoni in Venice from the Sea	BSTG, Inv.No.waf 137
1st half 18th C	Alessandro Magnasco Rocky Bay with Monks and Sailors	BSTG, Inv.No.2749
Wall Paintings		
1484–1490	D German Gothic ceiling painting	Cathedral St. Marien of Freiberg, Saxony
1499	D German Wall painting in the upper sacristy	Cathedral St. Marien of Freiberg, Saxony
c.1560	German Wall painting in the Moritz-Chapel	Cathedral St. Marien of Freiberg, Saxony
Sculptures		
c.1350	D German Seated Madonna Wood sculpture	Diocesan Museum, Freising
1497	Michael or Gregor Erhard Moerlin Epitaph Sandstone sculpture	Städtische Kunstsammlungen, Inv.No.1340
1502	Tilman Riemenschneider, Altar of the Holy Blood Wood sculpture	St. Jacob, Rothenburg ob der Tauber
1684–1689	Bernt Notke St. George Wood sculpture	Stockholm, St. Nikolai

II. Lead-tin yellow on paintings. Identified by R. J. Gettens, Washington, by microchemical tests.

15th C (attrib.)	Master of Flémalle Portrait of a Lady	Dumbarton Oaks, Washington
16th C (attrib.)	Tintoretto Baptism of Christ	Fogg Art Museum, Harvard Univ. 19.1949
16th C	School of Orcagna Scenes from the Life of Christ	Fogg Art Museum 1917.213
16th C	German School(?) Descent from the Cross	Fogg Art Museum 1912.46

III. Lead-tin yellow identified on paintings at the Institut Royal du Patrimoine Artistique, Brussels, by microchemical tests. (List contributed by J. Thissen.)

Date	Artist and Title	Gallery, Inventory No.
14th C	Anonymous manuscript, miniature book of hours	University of Ghent
15th C	Anonymous wall painting	Collégiale de Nivelles
15th C	Hieronymus Bosch Christ Carrying the Cross	MBA, Ghent
15th C	Hieronymus Bosch Heaven, Hell, and Purgatory	Musée Communal, Bruges
15th C	Aelbrecht(?), Dieric(?) Bouts Christ Crowned with Thorns	Pères de Seheut
15th C	Dieric Bouts Retable of the Holy Sacrament	Church of St. Peter, Louvain
15th C	Dieric Bouts and Hugo van der Goes Martyrdom of St. Hippolyte	Church of St. Sauveur, Bruges
15th C	Hugo van der Goes Death of the Virgin	Musée Communal, Bruges
15th C	Justus of Ghent Calvary	Cathedral of St. Bavo, Ghent
15th C	Master of Flémalle Trinity	Musée Communal, Louvain
15th C	Nabur Martinus wall painting The Nativity	Vleeshuis, Ghent
15th C	Hans Memling Triptych of Willem Moreel	Musée Communal, Bruges
16th C	Antonio de Solario Last Supper	Tongerloo, Church
16th C	Master of the Epiphany of Antwerp Adoration of the Magi	mrba, Brussels
17th C	Philippe de Champaigne Moses and Aaron in the Desert	Commission Assistance Publique, Brussels

MBA = Musées des Beaux Arts

MRBA = Musées Royaux des Beaux Arts

IV. Communicated by Joyce Plesters and Ashok Roy, National Gallery, London.

Date ^a	Artist and Title	Accession No./ Collection ^b	Lead–Tin Yellow Type
c.1300	Giotto ^c <i>Pentecost</i> Yellow–green background ^d	5360	II
c.1300	Giotto The Epiphany Yellow of center king's robed	Metropolitan Museum New York	II
after 1365(?)	Master of the Lehman Crucifixion Noli me Tangere Yellow lining of Christ's robed	3894	II
c.1365	Nardo di Cione Altarpiece: Three Saints In green of left-hand saint's robe. The lead-tin yellow is mixed with natural ultramarine and lead white ^d	581	II
c.1370/1371	Jacopo di Cione The Adoration of the Kings (panel from an altarpiece) Yellow tunic of figure far left ^d (see fig. 3A)	597	II
c.1455	Dieric Bouts The Entombment In the mixed greens of the landscaped	664	I
15th C, before 1475	Dieric Bouts The Virgin and Child Yellow highlights on background brocaded	2595	Ι
1473	Francesco del Cossa St. Vincent Ferrer Yellow highlight on rail behind the saint ^d	597	I
c.1490	Bergognone Altarpiece: The Virgin and Child with Sts. Catherine of Alexandria and Siena Lemon-yellow of Child's dress ^{e,f} (see fig. 2)	298	I
1501	Gerard David Canon Bernardinus de Salviatis and Three Saints Yellow design on St. Donatian's cloak ^d	1045	I

a. Information concerning dates of National Gallery pictures has been derived from the appropriate entries in the National Gallery catalogues.

b. Unless otherwise indicated, the accession numbers and collection are the National Gallery, London.

c. Catalogued as "ascribed to Giotto." See also table 2.

d. Identification by A. Roy using x-ray diffraction and spectrographic analysis with the laser microprobe.

e. Chemical identification by J. Plesters.

f. X-ray diffraction by R. J. Davies, Department of Mineralogy, British Museum (Natural History), London.

Date	Artist and Title	Accession No./ Collection ^a	Lead–Tin Yellow Type
1503	Raphael The Crucified Christ with the Virgin Mary, Saints, and Angels Sample from lemon-yellow highlight of pink and yellow changing drapery of female saint kneeling right; also highlights of deep golden drapery of flying angel, top righte.f	3943	I
1504	Cima The Incredulity of St. Thomas Yellow of disciple's robe	816	Ι
1505	Raphael St. John the Baptist Preaching Dark yellow jerkin ^d	6480	I
c.1508	Leonardo da Vinci The Virgin of the Rocks Sample from golden-yellow lining of the Virgin's blue cloake.f	1093	I
1512	Hans Baldung The Trinity and Mystic Pietà Sample from primrose-yellow sky between the heads of Christ and the Virgin	1427	I
c.1515	Raphael Cartoons for the Sistine Chapel tapestries Identified chemically on several areas of the various cartoons. One sample, from the pale yellow tunic of the man kneeling in the center foreground of <i>The Death of Ananias</i> was subjected to x-ray diffraction. It is of interest that although painted in a medium of animal glue, the lead–tin yellow	Collection of Her Majesty Queen Elizabeth II. On extended loan to the Victoria and Albert Museum, London	I
	shows no appreciable sign of having blackened in the London atmosphere ^{e,f}		
1519	Sebastiano del Piombo The Raising of Lazarus Yellow drapery of kneeling figure center foreground ^{e,f}	1	I
1520	Albrecht Altdorfer Christ Taking Leave of His Mother Pale yellow of skyd	6463	I
early 16th C	Master of Cappenberg Coronation of the Virgin Yellow highlight on carved post, right ^d	263	Ι
1523	Titian Bacchus and Ariadne Sample from pale primrose-yellow drapery beneath overturned urn at bottom left-hand corner of the picture ^{e,f}	35	I

Date	Artist and Title	Accession No./ Collection ^a	Lead–Tin Yellow Type
c.1530s(?)	Lorenzo Lotto The Prothonotary Apostolic, Giovanni Guiliano Yellow highlight on carpet ^d	1105	Ι
mid-1550s(?)	Titian Venus and Adonis Yellow of vased	34	I
c.1559	Titian The Death of Actaeon Highlight on foreground foliage	6420	Ι
c.1560	Tintoretto Miracle of the Loaves and Fishes Golden tassels on woman's scarfd	Metropolitan Museum New York	II
last quarter 16th C	Paulo Veronese Allegory of Love, II Yellow drapery ^d	1324	I
last quarter 16th C	Paulo Veronese Allegory of Love, III Primrose-yellow impasto on man's tunic ^d	1325	II
last quarter 16th C	Paulo Veronese Allegory of Love, IV Bright yellow of man's cloak. Yellow design from brocade pattern of woman's dress ^d	1326	II
c.1609	Peter Paul Rubens Samson and Delilah Primrose-yellow of flames, left edge ^d	6461	I
c.1620	Georges de La Tour The Cheat with the Ace of Clubs Pale yellow impasto on border of man's coatd	Kimbell Art Museum Fort Worth	I
1627	Hendrick ter Brugghen Jacob and Laban Yellow of lemon peel, foreground ^d	4164	II
c.1635	Rembrandt Belshazaar's Feast Pale yellow of writing on the wall ^d	6350	I
mid-17th C	Aelbert Cuyp A Distant View of Dordrecht Yellow-green impasto on foliage	962	I
1653	Rembrandt Aristotle with a Bust of Homer Yellow impasto on Aristotle's chaind	Metropolitan Museum New York	I
1689	Meindert Hobbema The Avenue, Middelharnis Warm pale yellow on canal bank. Highlight on foliaged	830	Ι

V. Communicated by Elizabeth H. Jones, Fogg Art Museum, Harvard University, Cambridge, Massachusetts.

Identification was done by x-ray diffraction and micro-beam probe.

Date	Artist and Title	Gallery, Inventory No.
(?)	School of Botticelli Madonna and Child	Fogg Art Museum No.1943.105
c.1525	Joos van Cleve Holy Family	Currier Gallery Manchester New Hampshire
signed and dated 1636	Jan van Goyen <i>Harbor Scene</i>	Fogg Art Museum, No.8.1959

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5

Smalt

BRUNO MÜHLETHALER and JEAN THISSEN

Current Terminology

English: smalt French: smalt (m.) German: Smalte (f.)

Italian: azzurro di smalto, smaltino

Spanish: esmalte Japanese: hana konjo

Obsolete Terminology and Synonyms

English: starch blue (seventeenth/eighteenth-century treatises); French: émail (*Encyclopédie Méthodique*, 1791; Watin, 1823) esmail (Van de Graaf, 1958), azur à poudrer (Watin, 1823), bleu d'émail; German: Kaiserblau, Königsblau, Azurblau (Schmid, 1857), Sächsischblau, Streublau, Couleur, Eschel (Winckler, 1959).

Composition

Smalt is a moderately finely to coarsely ground potassium glass of blue color. The blue is due to small but variable amounts of cobalt added as cobalt oxide during manufacture (see Chemical Composition).

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Preparation

The principal source of the cobalt used in the preparation of smalt in Europe since the time of the Middle Ages appears to have been the mineral smaltite ([Co,Ni]As₃₋₂), one of the skutterudite mineral series. In the seventeenth and eighteenth centuries the associated cobalt minerals erythrite ([Co,Ni]₃[AsO₄]₂.8H₂O) and cobaltite (Co,Fe)AsS were probably also used. The cobalt ore was roasted and the cobalt oxide (CoO) thereby obtained was melted together with quartz and potash or added to molten glass. When poured into cold water, the blue melt disintegrated into particles, and these were ground in water mills and elutriated. According to Beckmann (1846), who described in detail the methods employed in Saxony in the nineteenth century, several grades of smalt were made depending upon the cobalt content and the grain size.

The quality of the color (pleasantness of color [Winckler, 1959]) was marked by F (Fine), M (Medium), and O (Ordinary), respectively. The coarse grades received the label H (High), and were called, in Saxony, Streublau, which means, literally, blue to be strewn. Then followed the grades C (Couleur) and the fine ones E (Eschel, also Sumpfeschel). Beckmann further indicates that the complex Co-Ni-Fe-As ores from Saxony were first roasted, and much of the arsenic was volatilized. The oxides of cobalt (Co), nickel (Ni), and iron (Fe) were then melted together with siliceous sand, and the resulting products, called Zaffre or Zaffera, were, in part, sold to potters and glassmakers. The rest of the product was melted with potash and sand. In this way the cobalt passed into the slag, imparting to it a blue color.

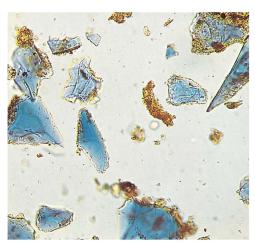


Fig. 1 Particles of smalt from a wall painting fragment from Kara Khoto in Inner Mongolia, eleventh-twelfth centuries. Mounted in Canada balsam, transmitted light, c. 335x. Photo: W. T. Chase.

When soda was used instead of potash, a violet tint was obtained.

History of Use

According to Beckmann (1846) and others (Ganzenmüeller, 1956; Winckler, 1959; Zimmermann, 1862), smalt was a European invention. Beckmann and Meltzer (1956) credit the discovery to Christoph Schürer, a Bohemian glassmaker, in about 1540-1560, but it was almost certainly available before the sixteenth century, as it has been detected in at least two European paintings of the fifteenth century (see Notable Occurrences). Riederer (1968), in a summary history of the pigment, notes a number of fifteenth-century references apparently to smalt, and points out that the material could have been obtainable in Europe considerably earlier. The European sources of information were reviewed by Gettens and Stout (1966) and more recently by Harley (1982). According to these later writers, smalt in some form was first produced several centuries before the alleged European discovery (Gettens & Stout, 1957–1958), perhaps in the Near East. It has been well established by Farnsworth and Ritchie (1938) and Neumann (1925) that cobalt ores were used for coloring glass in Egyptian and classical times. The origin of cobalt-tinted glass probably coincides with the development of vitreous enamel techniques, which are considered to be Near Eastern in origin. Enamels were made from easily fusible powdered and colored materials similar to glass.

It is understandable that a stable blue enamel powder should be used as pigment for painting. The very names, bleu d'émail and esmalte, indicate this. It is well known that in the past there was an important source of cobalt ores near Kashan in Iran, which was much employed over many centuries by the Persian potters and enamelers, and there is reason to believe that cobalt ores or oxides prepared from them were carried from central Iran over the trade routes to China as well as to the Near East. Gettens reported the presence of smalt in a fragment of a loess wall painting (Gettens & Stout, 1966) (the fragment is now in the study collection of the Freer Gallery of Art, Washington) given to him by the late Langdon Warner of Harvard University, who had brought it from the ancient site of Kara Khoto in Inner Mongolia (fig. 1). According to Warner, it dates from perhaps as early as the eleventh or thirteenth centuries. Gettens also observed smalt on later Chinese and Japanese paintings (see Notable Occurrences).

Occurrence of smalt on Japanese screen paintings of the sixteenth and seventeenth centuries raises an interesting question: Was the Japanese supply indigenous, or was it European in origin? It is widely known that cobalt in some form was used extensively in China as early as the Tang dynasty in order to make blue-colored ceramic glazes. Certainly smalt was known to the Venetian glassmakers as early as the fifteenth century (Laurie, 1914; Neumann, 1925). It seems to have been little used by Italian painters of the fourteenth and fifteenth centuries, perhaps because of the general availability of the superior pigments, ultramarine and azurite (see chapters 2 and 1); when those pigments became scarce in the seventeenth century, however, smalt was employed as a substitute, particularly in the skies and backgrounds of paintings where an intense blue was not needed. It was also used as a less costly pigment for wall decoration purposes (Littmann, 1886; Neumann, 1925). It is commonly found alongside the other traditional blue pigments in sixteenth-century Venetian paint-

Smalt was made in the Netherlands in the sixteenth century. It is frequently mentioned in the De Mayerne manuscript of the seventeenth century. Harley (1982) indicates the earliest British patent for making a pigment was a grant in 1605 to three Englishmen for the sole right to manufacture smalt for a period of twenty-one years. Smalt has been manufactured in England and even in Europe up to recent times as a ceramic glaze colorant. Manufacture by Reckitts Ltd. in England

ceased in 1952. A coarse grade of smalt was frequently used for strewing as a blue background (Littmann, 1886), especially in sign painting.

The arsenic content of samples containing smalt is sometimes revealed by spectrographic analysis, and appears to be particularly readily detected even at low concentrations by neutron autoradiography of pictures that contain the pigment (Ainsworth et al., 1982).

Potassium glasses are chemically less stable than sodium or lithium glasses (Cox et al., 1979). Stability also decreases with an increase in K₂O content. This may explain why several samples of smalt, on exposure to atmospheric conditions, have been seen to become pale and grayish (see Permanence and Compatibility: Discoloration); they also are slightly or readily soluble in dilute acids.

Chemical Composition

Table 1 Chemical Composition in Weight Percent

cations. The particles show conchoidal fracture
and typical thin, sharp edges of glass splinters
(fig. 2A and B). Tiny air bubbles have also been
observed within the particles and stress lines in the
glass may sometimes be seen (fig. 2B).

Optical Properties

The pigment is isotropic and therefore appears dark between crossed polars under the microscope. The refractive index is low and varies with composition (n = 1.46-1.55 for samples from wall paintings of the sixteenth and seventeenth centuries in Switzerland). Gettens and Stout (1966) give the refractive index at n = 1.49-1.52.

General Pigment Properties

Because smalt is a glass, its particles are transparent. Its hiding power is low, even lower than that of cobalt blue (cobalt aluminate). For this reason,

SiO ₂	K ₂ O	As_2O_3	CoO	Impurities*	Reference
66–72	10–21	0–8	2–18	Oxides of Ba, Ca, Na, Mg, Ni, Fe, Cu, Mn	(Winckler, 1959)
65–71	16–21		6–7	Al_2O_3	(Church, 1901)

^{*}These affect shade, hue, and purity of the blue color. Smalt, therefore, is not a definite chemical compound.

Particle Characteristics

The composition of smalt may vary considerably (see table 1). Because smalt is a coarsely ground glass, it can be recognized easily at low magnifi-

it must be coarsely ground for use as a pigment. According to De Wild (1929) the pigment, when used in oil-medium, has a tendency to settle and streak down perpendicular surfaces.

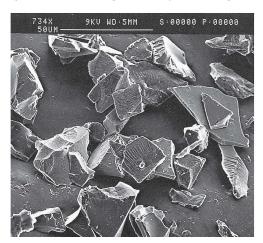
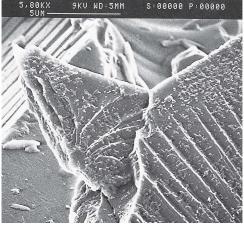


Fig. 2 Scanning electron micrographs of modern smalt, Reckitt's (Colours) Ltd., No. 4f10. Gold-coated. A. Printed at 492x.



B. Detail of the same sample, printed at 3,886x. Note the stress lines in the glassy particles. Photos: A Roy.

In common with other cobalt pigments (Simunkova et al., 1985), smalt exerts a powerful siccative effect on oil films. This property of smalt was appreciated quite early. For example, Félibien (1660), when speaking of drying oils, particularly those made by treatment with litharge, went on to say:

You can also make another sort by boiling with azur [smalt] in powder form, or enamel blue [also smalt] in nut oil. When it has all boiled, allow the oil to rest, and then pour it off. It is used for tempering white and other colors which are wanted to be kept very clean.

Color and Spectral Reflectance

A spectral reflectance curve in the visible region for a modern specimen of smalt is given in figure 3A with the derived chromaticity data.

The blue color of smalt arises principally from the presence of Co²⁺ ions held in a tetrahedral environment provided by the glass silicate matrix. A simple ligand field theory approach indicates that in tetrahedrally coordinated cobalt(II) (electronic structure 3d⁷), three absorption bands are to be expected, but their assignment is difficult (Patterson, 1967) (see fig. 3B). Smalt, like natural ultramarine, shows a strong rise in reflectance in the red (see fig. 3), whereas for azurite (see chapter 1) the red reflectance is low. Retouching matches for smalt are best made with artificial ultramarine or cobalt blue (Staniforth, 1985).

Permanence and Compatibility with Other Pigments and Media: Discoloration of Smalt

Smalt, like other glasses, is considered to be stable, unless it is improperly made (see Chemical Composition). It is better used in aqueous media and lime (fresco); in oil-media only a dull color is obtained because the refractive index of smalt is so close to that of dried oil.

Smalt in oil-media is often observed to have partially or completely discolored, although when lead white is mixed with the paint film, some protection against this loss of color is sometimes afforded. Plesters (1969) commented on this phenomenon and noted a number of paintings in the National Gallery, London, where the change in color of oil paint containing smalt has seriously disturbed the original color composition. Examples cited are: ascribed to Esteban Murillo, *The Adoration of the Shepherds* (no. 232) with smalt paint in the shepherd's jerkin (see figs. 4–6); El Greco's *The Adoration of the Name of Jesus* (no.

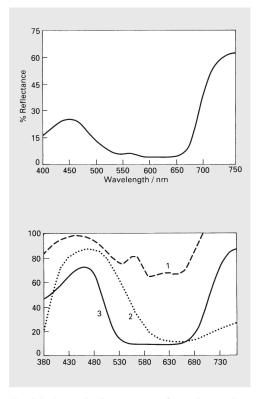


Fig. 3 A. Spectral reflectance curve for modern smalt in acrylic medium, 400-760 nm. CIE data: $L^* = 31.82$, $a^* = 14.03$, $b^* = -39.78$. Courtesy of D. Saunders.

B. Microspectrophotometric transmittance curves for three blue pigments used in Bouts' *The Entombment*, glue tempera on canvas, c.1455. National Gallery, London, No. 664. (1) Single smalt particle, (2) particle of azurite, (3) particle of natural ultramarine. The transmittance curve for smalt, even when pale-colored, is highly characteristic for this pigment and is readily distinguished from the traditional mineral blue pigments. Curves courtesy of Zeiss (Oberkochen) Ltd.

6260) in which discolored smalt is present in several of the draperies; and in the patchily discolored sky and foliage of Frans Hals' *Family Group in a Landscape* (no. 2285). The skies of Paolo Veronese's series of four *Allegories* (nos. 1318, 1324, 1325, and 1326) also seem to have suffered a similar change in the pigment to a greater or lesser degree.

It is pointed out that a number of factors, individually or in combination, may be implicated in the discoloration of the pigment (Plesters, 1969).

(a) The refractive index of smalt is low (c.1.46-

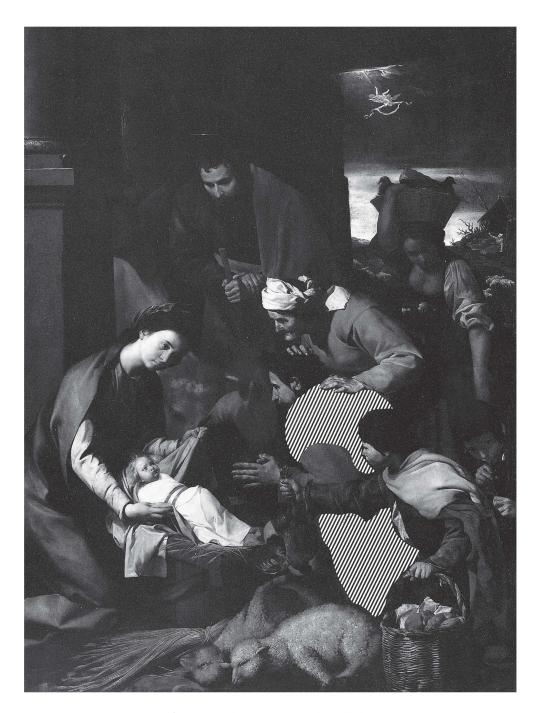


Fig. 4 Ascribed to Bartolomé Esteban Murillo, *The Adoration of the Shepherds*, canvas. National Gallery,

1.55), close to that of fresh linseed oil (c.1.48), so that as the refractive index of the oil film increases with drying and aging, the capacity for the smalt particles to scatter light in the paint film is di-

London, No. 232. The shaded areas indicate the discolored smalt paint of the shepherd's jerkin.

minished (see fig. 6). As it is a glass, smalt does not have a high tinting strength, so that if the refractive indices of pigment and medium are similar, and the oil-medium itself has discolored, the

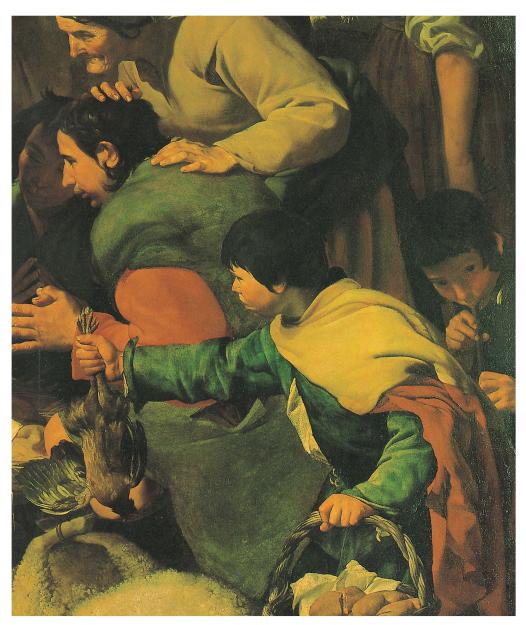


Fig. 5 Ascribed to Bartolomé Esteban Murillo, *The Adoration of the Shepherds*. National Gallery, London, No. 232. Detail showing the patchy discolored smalt

paint of the shepherd's jerkin corresponding to the shaded areas in fig. 4. Reproduced by permission of the Trustees.

original blue of the paint film will be affected by the color of the dried, darkened medium. Paintedout test samples confirm this observation.

(b) Because smalt is a potash glass, it is likely to be of lower stability than a soda glass. Some varieties may contain excess alkali, which is leached out into the surrounding paint medium, particularly as a result of exposure to atmospheric moisture, generating yellow or brown saponification products of the oil.

(c) Loss of the cobalt ion by migration from smalt particles and their subsequent interaction with the paint medium would account both for the diminution of color in the pigment and its apparent reac-

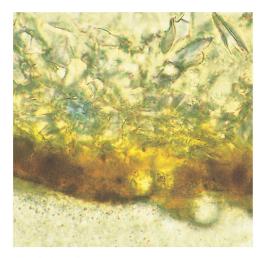


Fig. 6 Thin paint cross section showing discolored smalt in oil-medium from the glaze on the shepherd's jerkin in the Murillo shown in fig. 5. Transmitted light, 1,911x. Photo: A. Roy.

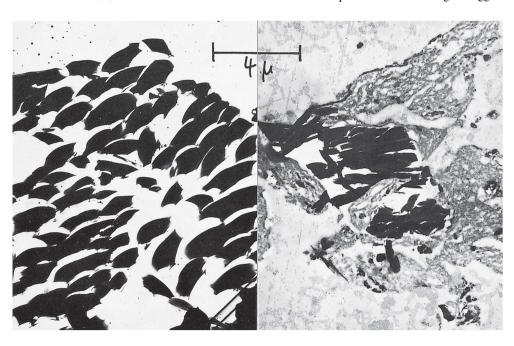
Fig. 7 Ultramicrotome thin sections of smalt. A. Unaltered smalt showing surviving characteristic conchoidal fracture, 5,500x.

B. Discolored smalt, 5,500x.

tivity with oil- or oleo-resinous media. Some confirmation of the dispersal of cobalt throughout the paint film has been obtained using the electron micro-beam probe on a cross section containing discolored smalt from Hendrik ter Brugghen's *The Singing Lute Player* (National Gallery, London, no. 6347) (Hornblower, 1963). In this context, it is interesting that smalt has been recommended in the eighteenth century as a siccative for other poor-drying blue pigments such as ultramarine and indigo when these are used in oil (Palomino, 1797).

Further studies have been carried out by one of the authors (Mühlethaler) and Giovanoli (1970), using a number of techniques. X-ray diffraction with the Nonius-de Wolff camera has clearly shown that the appearance of degraded smalt is not due to the formation of crystalline phases in the pigment. Electron microscopy of pure smalt particles and discolored particles by means of thin sections cut on the ultramicrotome indicates considerable interaction of the cobalt content of smalt with the paint medium, leaving a relatively unchanged core (fig. 7). Electron micrographs (fig. 8) show that the surface of an altered smalt particle is pitted and roughened at the grain boundary, presumably by chemical reaction of the alkali and/or the cobalt content of the pigment with the organic paint medium, usually in the case of smalt, a drying oil.

Reflectance spectra in the visible region suggest



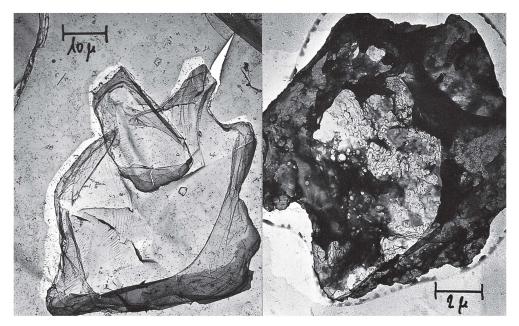


Fig. 8 Electron micrographs of smalt. Carbon replicas. A. Unaltered pigment, 1,120x. Note the conchoidal fracture.

B. Discolored smalt, 5,600x. The surface of the particle is clearly roughened in the degraded material.

the increased contribution of octahedral (six-fold) coordination of Co²⁺ in degraded smalt over the strong blue color imparted to the glass by tetrahedrally coordinated (four-fold) Co²⁺ (see fig. 9), but so far no mechanism for this process can be proposed.

Chemical Properties

Smalt is usually insoluble in cold 3M HCl, concentrated HNO₃, and 4M NaOH (Plesters, 1955–1956). Some specimens, however, have been observed that disintegrate in dilute hydrochloric acid. They may be high in potash and therefore already altered by moisture and carbon dioxide in the air. Alteration of smalt has been observed in several cases. Smalt melts at high temperatures (red heat) and by this means it can be distinguished from the infusible cobalt blue (cobalt aluminate).

Chemical Identification

Chemical tests for cobalt will not be applicable in many cases owing to the small sizes of samples that may be taken from art objects. Moreover, the low percentage of cobalt in the pigment matrix and because the material is a glass, makes the procedure time consuming. Plesters (1955–1956), on the other hand, found that the spot test reagents,

α-nitroso-β-naphthol and rubeanic acid, are practical for testing cobalt in comparatively tiny samples of smalt. Other microchemical tests for cobalt have been proposed in the literature—ammonium mercuric thicyanate (Pyantnitskii, 1966) and potassium nitrite (Augusti, 1949)—but their practicability in testing for cobalt in smalt is unknown.

Emission Spectrometric Identification

According to Farnsworth and Ritchie (1938), for the identification of cobalt in blue glasses, the two strong lines of the arc spectrum at 3453.5 and 3405.1 Å are accurately identifiable by comparison with spectra obtained from Hilger's *Raies ultimes* powder (1938; see also Gordon et al. [1953]). Hermann Kühn (private communication) at the Doerner Institute in Munich identified smalt solely by microscopic examination combined with emission spectrometric detection of cobalt lines: 2286.2, 3405.1, 3453.5, and 3529.8 Å.

Criteria for Certain Identification

Inquiry has shown that most analysts who deal with old paintings rely almost entirely on direct microscopic recognition based on particle and optical characteristics. As previously mentioned, a

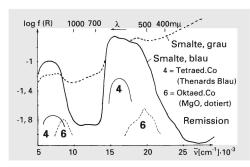


Fig. 9 Reflectance spectra in the visible region for unaltered and degraded smalt. The absorption bands indicated "4" and "6" are, respectively, characteristic of fourfold (tetrahedral) and sixfold (octahedral) coordination of cobalt(II).

sufficient sample is seldom available, especially from oil paintings, for microchemical detection of cobalt. A most useful confirmatory test is the identification of cobalt by emission spectrometry if the size of the sample permits. Arsenic is some-

times also detected in samples by this means, as well as by x-ray fluorescence analysis.

Provided the pigment grains are adequately separated, smalt can be distinguished microscopically from Egyptian blue and other blue pigments following the criteria in table 2.

X-ray Diffraction Analysis

Because smalt is a glass, it would not be expected to yield a diffraction pattern. Several samples examined by one of the authors have not shown any diffraction lines except for a weak halo in the low angle region.

X-ray Fluorescence Analysis

It is possible on a painting to carry out x-ray fluorescence analysis on the paint layer without taking a sample. This method was used by one of the authors several times to confirm the presence of smalt (after microscopical recognition) in fragments of mural paintings.

Table 2 Criteria for Distinguishing Smalt from Other Blue Pigments

	Refractive Index*	Color	Birefringence	Pleochroism	Fracture and Grain Appearance
Smalt	1.46-1.55	Pale to deep purplish blue	None	None	Conchoidal
Azurite	1.73–1.84	Pale to deep blue	Strong	Pale to deep blue	Irregular
Egyptian blue	1.61	More greenish blue	Strong	Blue to nearly colorless	Irregular
Cobalt blue	1.74	Pure rich blue	None	None	Irregular to rounded crusty surface texture
Cerulean blue	1.78	Greenish blue	None	None	Very fine rounded
Natural ultramarine	c.1.50	Purplish blue	None	None	Irregular
Artificial ultramarine	1.50-1.54	Purplish blue (less translucent than lapis lazuli)	None	None	Small, uniform, rounded compared with natural ultramarine

^{*}Distinction between smalt and other early blues is readily made in a mounting medium of moderately high refraction index, for example, Aroclor 5442 (n = 1.66), or similar media.

In some cases the concentration of cobalt in specimens of smalt is too low to give an unambiguous result using x-ray fluorescence (XRF), and the silicon content is insufficient positive proof of the use of the pigment. The possible presence of cobalt blue (cobalt aluminate) in a paint layer would also confuse the results of XRF analysis.

The principal detectable lines for cobalt are the $K\alpha$ line pair at 6.92 and 6.93 keV, and $K\beta$ fluorescence at 7.65 keV. It is not uncommon to detect arsenic and sometimes nickel impurities in specimens of smalt by XRF, and their presence tends to confirm the use of the pigment as opposed to the nineteenth-century pigments cobalt blue and cerulean blue (cobalt stannate).

Barbara H. Berrie (private communication) reports that XRF has been used at the National Gallery of Art in Washington to deduce the presence of smalt in Anthony Van Dyck's An Italian Noblewoman and Her Son (no. 1942.9.91), but failed to detect the pigment in Lodovico Carracci's Dream of St. Catherine of Alexandria (no. 1952.5.59), although it had been used in the painting mixed in small quantities with natural ultramarine.

Radioactive Methods of Identification

Using neutron activation analysis, cobalt can be detected in quantities as small as 5.10^{-12} g (Smales, 1966). Further references to this method are given by Pyantnitskii (1966, p. 137). Γ -spectroscopy as a further means of identification is also referred to by this author. To our knowledge, however, no application to smalt has been reported.

Terminal Date

None can be given because smalt has been manufactured from the uncertain time of its discovery to the present. Little seems to have been used by artists in Europe for easel painting after the discovery of Prussian blue in the early eighteenth century and especially since the discovery of synthetic ultramarine and cobalt aluminate blue (Thénard's blue) in the early nineteenth century. Joyce Plesters (private communication) reports that smalt was manufactured in England by Reckitts Ltd., up to 1952, but manufacture by that firm has now ceased.

Notable Occurrences

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
European Easel Paintings		
c.1455	Dieric Bouts The Entombment (mixed with azurite and ultramarine in Nicodemus' collar; glue tempera medium), National Gallery, London, No. 664	A.R. micr. + spectr.
c.1483	Michael Pacher <i>The Early Fathers</i> altar, BSTG, 2597–2600	H.K. micr. + spectr.
16th C	Pieter Breughel Census at Bethlehem, MRBA, Brussels	J.T. micr.
16th C	Pieter Breughel Massacre of the Innocents, MRBA, Brussels	J.T. micr.
mid-16th C	Parmigianino Madonna and Child and Saint Bruno, BSTG, 5289	H.K. micr. + spectr.

BSTG = Bayerische Staatsgemäldesammlungen, Munich

MRBA = Musées Royaux des Beaux Arts, Brussels

J.T. = Jean Thissen, Institut Royal du Patrimoine Artistique, Brussels

R.J.G. = Rutherford John Gettens, Freer Gallery of Art, Washington

E.W.F. = Elisabeth West FitzHugh, Freer Gallery of Art, Washington

J.P. = Joyce Plesters, National Gallery, London

A.R. = Ashok Roy, National Gallery, London

A.B. = Aviva Burnstock, National Gallery, London

H.K. = Hermann Kühn, Doerner Institut, Munich

B.M. = Bruno Mühlethaler, Swiss National Museum, Zurich

micr. = Identification with the microscope

spectr. = Identification with the emission spectrograph chem. = Identification by microchemical tests

edx. = Energy-dispersive x-ray microanalysis

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
c.1556	Tintoretto Christ Washing His Disciples' Feet (beneath ultramarine in foreground blue drapery), National Gallery, London, No. 1130	J.P. micr.
c.1560	Titian Madonna and Child in an Evening Landscape, BSTG, 464	H.K. micr. + spectr.
2nd quarter 16th C	Tintoretto Vulcan Surprising Venus and Mars, BSTG, 9257	H.K. mier.
c.1560	Tintoretto Crucifixion, BSTG, 4590	H.K. micr. + spectr.
1561–1562	Paolo Veronese <i>The Consecration of St. Nicholas</i> (in discolored patch of sky and in dark shadows of blue drapery), National Gallery, London, No. 26	J.P. micr.
1570s(?)	Paolo Veronese The Family of Darius before Alexander (gray-blue sky), National Gallery, London, No. 294	A.R. micr.
before 1579	Tintoretto Gonzaga Cycle. 1st Row: <i>The Relief of Legnano</i> , BSTG, 7307	H.K. micr. + spectr.
before 1579	Tintoretto Gonzaga Cycle. 1st Row: <i>Battle of Legnano</i> , BSTG, 7304	H.K. micr. + spectr.
1579–1580	Tintoretto Gonzaga Cycle. 2nd Row: Entry of Philip II into Mantua, BSTG, 7302	H.K. micr. + spectr.
2nd half 16th C	Paolo Veronese <i>The Vision of St. Helena</i> (from discolored gray–blue of sky), National Gallery, London, No. 1041	J.P. micr.
c.last quarter 16th C	Paolo Veronese Four <i>Allegories</i> (in discolored gray–blue of sky of each), National Gallery, London, Nos. 1318, 1324, 1325, 1326	J.P./A.R. micr. + spectr.
last quarter 16th C	El Greco The Adoration of the Name of Jesus (in discolored blue drapery), National Gallery, London, No. 6260	J.P. micr.
late 16th and 17th C	Unknown Scottish artists In several series of painted decorations on the wood ceilings of Scottish Castles, of which the best known is Crathes Castle. As the principal blue pigment in a medium of animal glue. National Trust for Scotland	J.P. micr. + chem.

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
c.1605	Johann George Fischer Duke Ludwig of Bavaria Starting the Crusade, BSTG, 3747	H.K. micr. + spectr.
c.1610	Abraham Janssens van Nuyssen Diana with Her Nymphs, BSTG, 13111	H.K. micr. + spectr.
2nd decade 17th C	Abraham Janssens van Nuyssen Mount Olympus, BSTG, 4884	H.K. micr. + spectr.
1620/1621(?)	Anthony van Dyck <i>A Woman and Child</i> (blue–gray highlight on skirt), National Gallery, London, No. 3011	A.R. micr.
1st quarter 17th C	Domenico Fetti Ascension of Mary, BSTG, 9340	H.K. micr. + spectr.
1st quarter 17th C	Sebastian Vrancx The Surprise Attack, BSTG, 6295	H.K. micr. + spectr.
1624	Hendrick ter Brugghen The Singing Lute Player (from blue ribbons decorating sleeve; also darker blue drapery in bottom right corner), National Gallery, London, No. 6347	J.P. micr. Also by electron micro-beam probe analysis (Hornblower, 1953)
c.1624–1625	Peter Paul Rubens The Apocalyptic Wife, BSTG, 891	H.K. micr. + spectr.
1627	Hendrick ter Brugghen Jacob and Laban (Leah's blue dress), National Gallery, London, No. 4164	A.R. micr. + spectr.
1630s	Anthony van Dyck <i>Equestrian Portrait of Charles I</i> (blue sky), National Gallery, London, No. 1172	J.P. micr.
c.1635	Peter Paul Rubens Meleager and Atlanta, BSTG, 355	H.K. micr. + spectr.
1631	Paulus Moreelse <i>Madonna and Child</i> , BSTG, 6343	H.K. micr. + spectr.
1637	Anthony van Dyck Lady Thimbelby and Viscountess Andover (gray-blue sky), National Gallery, London, No. 6437	A.R. micr.
1636–1638	Rembrandt Belshazzar's Feast (from gray-blue background), National Gallery, London, No. 6350	A.R. micr. + spectr. (see Bomford et al., 1988)
1640s(?)	Jan van Goyen <i>A River Scene</i> (blue sky), National Gallery, London, No. 6154	A.R. micr.
1st half 17th C	Ascribed to Bartolomé Esteban Murillo <i>Adoration of the Shepherds</i> (from discolored greenish gray jerkin of shepherd [see figs. 4, 5, and 6]), National Gallery, London, No. 232	J.P. micr. + chem.

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
2nd quarter 17th C	Johann Ulrich Loth The Holy Family, BSTG, 7373	H.K. micr. + spectr.
2nd quarter 17th C	Johann Ulrich Loth The Judgment of Solomon, BSTG, 2566	H.K. micr. + spectr.
2nd quarter 17th C	Johann Ulrich Loth The Holy Family in the Open, BSTG, 3737	H.K. micr. + spectr.
mid-17th C	Karel du Jardin Self-Portrait (in various underlayers), National Gallery, London, No. 1680	A.R. micr.
mid-17th C	Aelbert Cuyp A Herdsman with Cattle Near Dordrecht (sky), National Gallery, London, No. 962	A.R. micr.
1644	Claude Lorrain A Seaport (sky), National Gallery, London, No. 5	A.R. micr. + spectr.
1648	Claude Lorrain Seaport: The Embarkation of the Queen of Sheba (sky), National Gallery, London, No. 14	A.R. micr. + spectr.
17th C	Anthony van Dyck Mystic Marriage of St. Catherine, Fogg Museum of Art, Harvard University, No. L7693	R.J.G. micr.
c.1650	Velázquez The Toilet of Venus (The "Rokeby Venus") (from blue–gray drapery, also blue shadows of flesh), National Gallery, London, No. 2057	J.P. micr.
c.1650	Frans Hals Family Group (from discolored pale blue of sky and in browned foliage), National Gallery, London, No. 2285	J.P. micr.
1653	Rembrandt Aristotle with a Bust of Homer (in skirt of apron), Metropolitan Museum of Art, New York	J.P./A.R. micr. + spectr.
1654	Gerard Dou Old Woman Selling Vegetables and Herrings, BSTG, 552	H.K. micr. + spectr.
c.1655	Jan Vermeer Diana with Her Companions, Mauritshuis, Den Haag	H.K. micr. + spectr.
c.1656	Jan Vermeer Sleeping Girl, Metropolitan Museum of Art, New York	H.K. micr. + spectr.
1656	Jan Vermeer The Procuress, Gemäldegalerie, Dresden	H.K. micr. + spectr.

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
c.1659	Jan Vermeer Street in Delft, Rijksmuseum, Amsterdam	H.K. micr. + spectr.
c.1660	Jan van Coxie Landscape with Figures, Fogg Museum of Art, Harvard University, No. 1964.67	R.J.G. micr.
1662	Karel du Jardin The Conversion of Saul (as a minor constituent of the ultramarine blue paint of the cloak of Saul), National Gallery, London, No. 6296	J.P. micr.
c.1663	Jan Vermeer Girl with Wineglass, Herzog-Anton-Ulrich Museum, Brunswick	H.K. micr. + spectr.
1660(?)	Jan van de Cappelle A River Scene with a Large Ferry (sky), National Gallery, London, No. 967	A.R. micr.
1663	Rembrandt Equestrian Portrait (sky and horse's flank), National Gallery, London, No. 6300	A.R. micr.
17th C	Salomon van Ruisdael Seascape, Fogg Museum of Art, Harvard University, No. 1335.29	R.J.G. micr.
17th C	Attributed to Jacob van Ruisdael <i>The Old Oak</i> , Fogg Museum of Art, Harvard University, No. 1966.32	R.J.G. micr.
1668	José Antolinez Maria Immaculata, BSTG, 7716	H.K. micr. + spectr.
c.1670	Nicolaes Berchem Gypsy Camp, BSTG, 6313	H.K. micr. + spectr.
1671/1672	Claude Lorrain Landscape: Aeneas at Delos (beneath ultramarine in the sky), National Gallery, London, No. 1018	A.R. micr.
3rd quarter 17th C	Salvator Rosa Landscape with Mercury and the Dishonest Woodman (dull blue sky), National Gallery, London, No. 84	A.R. micr.
3rd quarter 17th C	Lucas Achtschellinck Mountain Scene, BSTG, 6515	H.K. micr. + spectr.
3rd quarter 17th C	Barent Gael Peasant Scene, BSTG, 6402	H.K. micr. + spectr.
3rd quarter 17th C	Hendrik Mommers Roman Market, BSTG, 6396	H.K. micr. + spectr.
3rd quarter 17th C	Frederick de Moucheron Landscape with Waterfall, BSTG, 6549	H.K. micr. + spectr.
3rd quarter 17th C	Eglon Hendrick van der Neer <i>Genre</i> , BSTG, 6449	H.K. micr. + spectr.

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
3rd quarter 17th C	Adam Pynacker Landscape with Ruins, BSTG, 6520	H.K. micr. + spectr.
1680	Caspar Netscher <i>Young Cavalier</i> , BSTG, 6323	H.K. micr. + spectr.
1689	Meindert Hobbema The Avenue, Middleharnis (sky), National Gallery, London, No. 830	A.R. micr.
1692	Monogrammist: BA Wolf and Lamb, BSTG, 3422	H.K. micr. + spectr.
2nd half 17th C	Willem de Heusch Landscape at Sunset, BSTG, 6442	H.K. micr. + spectr.
17th C	Peter Paul Rubens Descent from the Cross, Cathedral of Antwerp	J.T. micr.
17th C	Peter Paul Rubens Minerva Defeating the Discorde, MRBA, Brussels	J.T. micr.
17th C	J. B. de Saire Saint Amelurga, Eglise Notre Dame, Tamise	J.T. micr.
17th C	Rembrandt Storm on Galilee, Isabella Stewart Gardner Museum, Boston	R.J.G. micr.
17th C	Rembrandt Jacob Fighting with the Angel, Gemäldegalerie, Berlin	J.T. micr.
17th C	David Teniers Saint Hilduardus, Eglise Notre Dame, Termonde, Belgium	J.T. mier.
last quarter 17th C	Sassoferrato The Virgin and Child Embracing (mixed with ultramarine in the sky), National Gallery, London, No. 740	A.R. micr.
c.1700	Godfried Schalken Rest on the Flight to Egypt, BSTG, 1294	H.K. micr. + spectr.
c.1700	Michel Willman Christ Mourned, BSTG, 13163	H.K. micr. + spectr.
1709	Jan van Huysum Fruits, Flowers and Insects, private collection, Paris	H.K. micr. + spectr.
1743	William Hogarth Shortly after the Marriage (blue–green carpet), National Gallery, London, No. 114	A.R. micr.
1750	Christian Wilhelm Ernst Dietrich Ideal Landscape with Thunderstorm, BSTG, 6283	H.K. micr. + spectr.

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
1770/1772	Joseph Wright of Derby Mr. and Mrs. Coltman (mixed with vermilion, charcoal black, and white for the pinkish mauve sky), National Gallery, London, No. 6496	A.R. micr.
c.1811	Caspar David Friedrich Winter Landscape with a Church (pale bluegray sky), National Gallery, London, No. 6517	A.B. micr. + edx.
Wall Paintings		
11th–13th C	Wall painting fragment from Kara Khoto in Central Asia recovered by the Harvard-Fogg Museum Expedition in 1925. Freer Gallery of Art, Washington, SCA-PA-143abc	R.J.G. micr.
1325–1453	Wall painting in the Kariye Çamii (formerly Byzantine Church of Our Saviour Monastery of the Chora, Istanbul); in the blue–gray underrobe on the second figure on the left in the S.E. Arcosolium, Monastery of Chora, Istanbul	R.J.G. micr. (Gettens & Stout, 1957–1958)
1376–1644	Seated Buddha Ming dynasty mud wall painting, Fogg Museum of Art, Harvard University, 1933.190	R.J.G. micr.
c.1508	Giorgione and Titian Fresco fragment depicting nude figures. Recently detached from the Wall of the Fondaco dei Tedeschi, Venice, and now in the collection of the Accademia Gallery; deep blue drapery. Accademia, Venice	J.P. micr.
1590–1636	Giovanni da San Giovanni (Manozzi) Fresco fragment. Mixed with terre verte in the background. Fogg Museum of Art, Harvard University, No. 1937.24	R.J.G. micr.
1615	Guercino (Giovanni Francesco Barbieri) Wild Landscape with a Hunter Shooting Ducks. Pinacoteca Civica, Cento (transferred fresco), Guercino Exhibition, Bologna 1968, Catalogue No. 18A	J.P. mier.
1615	Guercino (Giovanni Francesco Barbieri) Extraction of Hemp by Retting. Pinocateca Civica, Cento (transferred fresco), Guercino Exhibition, Bologna 1968, Catalogue No. 18E	J.P. micr.
c.1618	Guercino (Giovanni Francesco Barbieri) David with the Head of Goliath. Thomas Agnew & Sons Ltd., London (fresco and plaster applied to wood panel), Guercino Exhibition, Bologna 1968, Catalogue No. 24	J.P. micr.

Date	Artist, Title, Description, Collection or Location	Analyst and Method of Identification
17th and 18th C	Unknown artists Several decorative wall paintings. In baroque churches in Switzerland	B.M. micr.
1770	Franz Ludwig Hermann Wall painting, Klosterkirche, Kreuzlingen, Switzerland	B.M. micr.
Far Eastern Scroll and Scre	en Paintings	
17th C Japanese	Ogata Korin (1655–1716) Flowers and Rocks, Freer Gallery of Art Washington, No. 00.59	R.J.G. micr.
late 17th to mid-19th C	Ukiyo-e School paintings (27 paintings), Freer Gallery of Art Washington	E.W.F. and R.J.G. micr. (FitzHugh, 1979)
18th C Japanese	Bungaku (Ukiyo-e School) A Puppet Show, Freer Gallery of Art, Washington, No. 98.505	R.J.G. micr.
18th C Japanese	Utamaro Ukiyo-e (1754–1806) Moonlight Revelry at Sagami Dozo, Freer Gallery of Art, Washington, No. 03.54	R.J.G. micr.
?	Miscellaneous On red silk fabric on wood figure. San Miguel Church, Santa Fe, New Mexico	R.J.G. micr.

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Verdigris and Copper Resinate

HERMANN KÜHN

A. Verdigris

Current Terminology

English: verdigris French: vert-de-gris German: Grünspan Italian: verderame

Spanish: cardenillo, verdete

Obsolete Terminology and Synonyms

Verdigris is mentioned in Greek and Roman literature sources: Theophrastus (Hill, 1774) and Dioscorides (Matthiolus, 1655) wrote about ιοζ (ιοζχαλκον, rust of copper); Pliny (König, n.d.) called it aerugo and Vitruvius (Fensterbusch, 1964) called it aeruca. While in current usage the term verdigris refers exclusively to copper salts of acetic acid (copper acetates), the classical writers used the words ιοζ and aerugo (aeruca) to denote various blue-green and green corrosion products formed at the surface of copper, copper alloys, and copper ores. Pliny, for example, mentioned that aerugo can be scraped from natural copper ore (König, n.d.). Theophilus described a viride hispanicum and a viride salsum (Dodwell, 1961). The viride hispanicum is composed of copper salts of acetic acid, hence verdigris, while the viride salsum is formed when copper covered with honey and salt is exposed to the vapors of urine or acetic acid. It thus comprises either a mixture of basic copper chlorides and copper carbonates or a mixture of basic copper chlorides and copper acetates. (These salts were produced at the Doerner Institute and identified by x-ray diffraction.) The composition of the viridis color cum sale, described

by Heraclius (Ilg, 1873), corresponds to that of viride salsum. The viride cupri vel aeris, also described by Heraclius, is identical to verdigris, as also is the viride grecum, mentioned in the Mappae Clavicula (Philipps, 1847). The viride rotomagense, that is, green after the manner of Rouen, mentioned in the Mappae Clavicula, consists of copper acetates (verdigris) and small quantities of copper salts of fatty acids. It is formed when soaptreated copper plates are exposed to acetic acid vapor for a reasonable length of time. In Italian literature, verdigris is denoted as verderame or verde eterno and in Spanish literature as verdete or cardenillo (Palomino, 1715). According to Merrifield (1849), the English word verdigris and the French term vert-de-gris are probably derived from vert de Grèce (viride graecum). Both the German word Grünspan and the Dutch term Spaans groen may be related to Spanisch Grün (translation from viride hispanicum) or to the preparation of verdigris from copper filings.

For designation of special types of verdigris, such as "crystallized," "crude," "French," and so on, see Chemical Composition and Properties.

History of Use

Pliny, in *Naturalis Historia* (König, n.d.), mentioned that verdigris (*aerugo*) was often used as a pigment in antiquity. Although Raehlmann (1914) found copper in numerous green and grayish green paint samples of paintings from Rome and Pompeii, he could not establish whether these samples contained verdigris or malachite. In color lists and in the literature on the technique of painting through the Middle Ages and the Renaissance and baroque periods, verdigris is often mentioned.

Examination of paintings has confirmed that verdigris was used as a pigment by European painters from the thirteenth to the nineteenth centuries (see Notable Occurrences). Verdigris is most often found on easel paintings of the fifteenth to the seventeenth centuries. In Early Italian, Early Netherlandish, and Early German paintings, verdigris was widely used as the green pigment to produce intense pure green tones for landscapes and drapery, because neither mixtures of blue and yellow pigments nor the other green pigments known at the time, that is, malachite and green earth, possessed such strong color. A common device was to glaze over an opaque body color of lead white combined with verdigris, or sometimes verdigris mixed with lead-tin yellow, with a copper resinate layer to produce a deep saturated green.

Verdigris is rarely found in eighteenth- and nineteenth-century paintings. This may be because there was no longer any special need for this bright green in the eighteenth century, and moreover that emerald (Schweinfurt) green, a pigment hardly surpassable in its brightness, and subsequently, viridian, were available as early as the nineteenth century. However, it is interesting to note that verdigris in oil-medium as a tube-color was available in France as late as 1928 (Lefranc, 1928).

Verdigris was used both in glazes and in opaque paint layers. The latter contain, as a rule, high refractive index additives of lead white and/or lead—tin yellow because, without these additives, verdigris has poor hiding power in oil-media.

In addition, lead-tin yellow changes the bluish green of verdigris to a warmer, more neutral green. For the application of verdigris as a drying agent in oil-media, see General Pigment Properties.

Preparation

Basic verdigris (see Chemical Composition and Properties) was especially prepared in wine growing areas—for example, from the twelfth century in the neighborhood of Montpellier in the South of France—by piling up winemarc and copper plates and subjecting them to a process of fermentation. Interestingly, verdigris production centered at Montpellier had become almost exclusively a women's industry by the eighteenth century, using copper imported from Sweden (Benhamou, 1984)

Under the influence of the acetic acid formed during the process, the copper becomes covered with blue and blue–green crusts, which are then scraped off. This preparation of verdigris from the waste products of winemaking had already been described by the classical writers (see Hill, 1774; Matthiolus, 1655; König, n.d.; Fensterbusch, 1964).

According to medieval recipes, copper strips are attached to a wooden block containing acetic acid, and the sealed block is then buried in dung. Some weeks later, the verdigris is scraped from the copper strips and the process is repeated (Dodwell, 1961).

In experiments at the Doerner Institute, this procedure usually yielded a mixture of basic and neutral verdigris. To purify the verdigris scraped from the copper, it is often dissolved in strong acetic acid. The neutral copper acetate, which separates from the solution in the form of crystals, is called "crystallized" or "distilled" verdigris. From the early nineteenth century, verdigris has also been made by reacting a copper sulfate solution with solutions of lead, barium, or calcium acetate, in which insoluble lead, barium, or calcium sulfate precipitates and copper acetate remains in solution. A detailed description of the various procedures for the preparation of verdigris can be found in Gentele's Lehrbuch der Farbenfabrikation (Buntrock, 1909).

Chemical Composition and Properties

Verdigris is a collective term for copper acetates of different chemical composition, which range in color from green, via green-blue and blue-green, to blue. When heated in the dry state, copper acetates decompose to black cupric oxide, water, and acetic acid. Copper acetates dissolve in dilute mineral acids. Alkalies convert them into blue copper hydroxide. Oils, resins, and proteins react with copper acetates to form green transparent copper oleates, resinates, and proteinates (see also General Pigment Properties). The composition, preparation, and properties of the various copper acetates were extensively described by Gauthier (1958). On the basis of their chemical composition, the numerous kinds of verdigris can be divided into two groups—basic and neutral verdi-

Basic verdigris is formed when acetic acid vapor, water vapor, and air act on copper and copper alloys (fig. 1). Usually, it was sold in blue, or partly blue—green, marbled lump form (fig. 2), which, if pulverized, produced a light blue powder. It was designated as verdigris "from Montpellier," "from

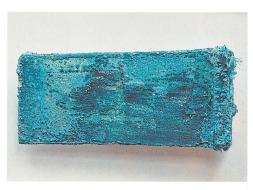


Fig. 1 Blue basic verdigris grown over a period of some months on copper foil in an atmosphere containing acetic acid.



Fig. 2 Blue basic verdigris was formerly sold in the form of blue lumps. The verdigris shown comes from an old pharmaceutical collection of the nineteenth century.

Grenoble," or as "French," "English," "German," "Swedish," "ordinary," or "crude" verdigris. These designations do not necessarily refer either to the place of origin or to the method of preparation.

According to Gauthier (1958), basic verdigris can contain the following copper acetates:

(1) [Cu(CH ₃ COO) ₂] ₂ .Cu(OH) ₂ .5H ₂ O	blue
(2) $Cu(CH_3COO)_2$. $Cu(OH)_2$. $5H_2O$	blue
(3) $Cu(CH_3COO)_2$. $[Cu(OH)_2]_2$	blue
(4) $Cu(CH_3COO)_2$.[$Cu(OH)_2$] ₃ .2 H_2O	green

The preparation of these compounds was also described by Schweizer and Mühlethaler (1968). Verdigris can be composed of one of these acetates alone or of mixtures of acetates (1) and (2), or (2) and (4). Acetate (3) can only occur on its own, because on the basis of phase diagrams it is unstable in mixtures with the other acetates (Gauthier, 1958). A basic verdigris prepared at the

Doerner Institute (fig. 1) proved to be acetate (1), when the x-ray diffraction powder pattern was compared with those for standards synthesized at the Swiss Landesmuseum in Zürich under the direction of Bruno Mühlethaler, and a basic verdigris from the nineteenth century proved to be acetate (2) (fig. 2). Blue basic verdigris is only slightly soluble in cold water, but it decomposes in hot water, turning brown. Acetic acid dissolves basic verdigris with the formation of a dark green color, the product being neutral copper acetate Cu(CH₃COO)₂.H₂O.

Neutral verdigris, also called verde eterno, "crystallized," "distilled," or "purified" verdigris, is neutral copper acetate Cu(CH₃COO)₂.H₂O, which is formed when the basic acetates are dissolved in acetic acid. Neutral copper acetate is also formed when basic verdigris is ground with strong acetic acid, as recommended, for example, by Cennino (Thompson, 1954) (see also General Pigment Properties). Neutral verdigris is composed of blue–green crystals which dissolve entirely without decomposition in water. Decomposition only occurs when the solution is boiled. Neutral verdigris dissolves in acetic acid, producing a dark green solution.

Particle Characteristics

Neutral verdigris is composed of tabular crystals with rhombic and hexagonal faces and distinct boundaries (see fig. 5A). The crystals frequently grow together and twin structures also occur (fig. 3). Blue basic verdigris often consists of bundles of fine needles (figs. 4 and 5E). Basic verdigris, which was formerly sold in lump form, often shows no characteristic crystalline form when viewed under the microscope.

Some transmission electron microscope (TEM) micrographs of verdigris samples were published by Schweizer and Mühlethaler (1968).

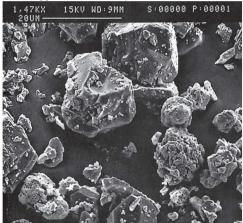
Optical Properties

Under the polarizing microscope with parallel polarizers, neutral verdigris shows a clear pleochroism from light pale green to a full dark blue. According to Merwin (1917), the refractive index for α is 1.53 and for γ , 1.56. In Canada balsam (n=1.53), neutral verdigris shows no relief. The single crystals are strongly birefringent. Blue basic verdigris has largely the same optical properties as neutral verdigris.

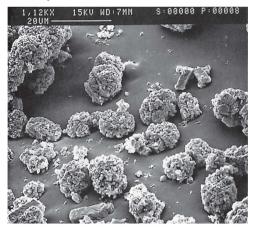


Fig. 3 Neutral verdigris. Transmitted light, c. 325x.

Fig. 5 Scanning electron micrographs of neutral and basic copper acetates (verdigris).



A. Neutral copper acetate. British Drug Houses. Goldcoated, printed at 1,044x.



C. Anhydrous neutral copper acetate. Early twentieth-century sample. Gold-coated, printed at 795x.

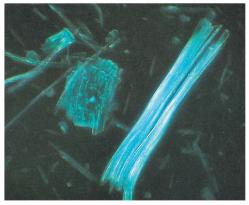
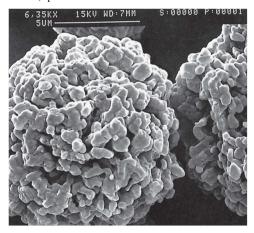


Fig. 4 Blue basic verdigris grown in the course of some months on copper foil in an atmosphere containing acetic acid, c. 325x.



B. Neutral copper acetate. Andrew Baird Ltd. Goldcoated, printed at 302x.



D. Detail of the same specimen as in C. Gold-coated, printed at 4,509x.



E. Blue basic verdigris: [Cu(CH₃COO)₂]₂.Cu(OH)₂.5H₂O. Prepared by B. Mühlethaler. Gold-coated, printed at 2,329x.



F. Blue basic verdigris: Cu(CH₃COO)₂.[Cu(OH)₂]₂. Prepared by B. Mühlethaler. Gold-coated, 2,989x.



G. Green basic verdigris: Cu(CH₃COO)₂.[Cu(OH)₂]₃.2H₂O. Prepared by B. Mühlethaler. Gold-coated, printed at 580x.



H. Detail of the same specimen as in G. Note the stacked tabular crystal form. Gold-coated, printed at 1,377x. All photos by A. Roy.

General Pigment Properties

A remarkable property of verdigris paints is that they are subject to a color change from blue-green to green (fig. 6A and B). In the first month, this color change is fairly pronounced, but after that, the rate of change decreases; hence, paints that are several months old undergo little further change. The magnitude of the color change depends on the kind of verdigris (basic or neutral) and the kind of binding medium, as shown in table 1.

The color change to green is less pronounced

with neutral verdigris in oil and egg tempera than it is with basic verdigris. This suggests that neutral verdigris was preferred as a pigment. In the literature on painting techniques (Thompson, 1954; Van de Graaf, 1958), recommendations are found for the grinding of verdigris with vinegar before use, thus converting basic to neutral verdigris. Verdigris reacts with binding media; with resins it forms copper resinates (see B. Copper Resinate); with oils, it forms copper oleates; and with proteins, it forms copper—protein compounds

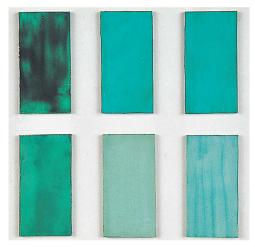
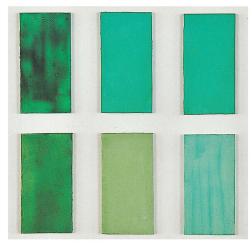


Fig. 6 A. Verdigris paints, one day old. *First row*: neutral verdigris. *Second row*: basic verdigris. In all cases the medium is linseed oil, egg tempera, and gum arabic (left to right).

Table 1 Reflectance Maxima of Verdigris Paints

Linseed Oil	Egg Tempera	Gum Arabic
500 nm	500 nm	500 nm
500 nm	500 nm	500 nm
512 nm	506 nm	506 nm
490 nm	490 nm	490 nm
500 nm	508 nm	502 nm
521 nm	528 nm	504 nm
	500 nm 500 nm 512 nm 490 nm 500 nm	Oil Tempera 500 nm 500 nm 500 nm 500 nm 512 nm 506 nm 490 nm 490 nm 500 nm 508 nm

(Flieder, 1968). It has been shown that verdigris exhibits a pronounced anti-oxidant effect on linseed oil films (Rasti & Scott, 1980) as well as protecting the non-saponifiable fractions of drying oils (Mills & White, 1975). In addition, verdigris promotes the drying of oil-media, a property that is emphasized in the literature. Félibien (1660) wrote of verdigris, "It is used because it dries very well, and one mixes only a little into the blacks which by themselves never dry." Similarly, Palomino (1715) wrote, "The best drying agent is, however, verdigris ground in oil [cardenillo merlido à el olio], especially for red and black paints; with red paints, one should be very sparing with verdigris. The amount of verdigris to be added de-



B. Verdigris paints, three months old. Arrangement of the paint layers as in A.

pends on how much the painter wishes to use, and varies from the size of a hazel-nut to a pin's head." Armenini (1586) made a similar point with regard to the drying of black pigments when he recommended the addition of verdigris in oil mixed with resin varnish.

Cennino described a cement for faience—made from linseed oil to which white lead and verdigris are added as drying agents—and a mordant for gold leaf, containing the same drying agents (Thompson, 1954; Bomford et al., 1989).

Permanence and Compatibility with Other Pigments

In the literature on painting from earlier centuries, it is often pointed out that verdigris is unstable, its use leads to deterioration of other pigments, and it can only be used under very special conditions which should be strictly followed (Thompson, 1954; Van de Graaf, 1958). However, experiments with paint specimens and observations on paintings—the results of which are summarized in this section—show that the properties of verdigris are not nearly as harmful as suggested by the literature.

Compatibility with Other Pigments

Many of the verdigris areas found in paintings contain additions of lead white and/or lead—tin yellow (see Notable Occurrences) and do not manifest any harmful alterations to the paint quality. A

mixture of verdigris with yellow arsenic sulfide (orpiment) in an oil-medium has remained similarly unchanged (see Notable Occurrences). Verdigris paints containing lead white and lead-tin yellow that were subjected to artificial aging at elevated temperature showed no difference in behavior when compared with pure verdigris paints. However, mixtures of verdigris with sulfur-containing pigments (for example, ultramarine and arsenic sulfide) in aqueous media may darken due to the formation of copper sulfide.

Fastness to Light

Prepared specimens of basic and neutral verdigris in linseed oil and egg tempera were exposed to fluorescent tubes, xenon lamps, and mercury vapor lamps for three months at a high illumination level. After this period, the paint specimens showed little difference in color when compared to paint films that had been exposed under normal lighting conditions for the same length of time. This shows beyond doubt that verdigris paints have good lightfastness.

It is often noted that in early paintings certain areas of green show a strong brown discoloration at the surface. This discoloration is less pronounced where the paint surface is covered, for instance beneath the frame, than where it is fully exposed to light. The reasons for such discoloration can, at present, only be surmised (see also Copper Resinate, Permanence). It has been established, however, that this color change is not due to decomposition of verdigris under the influence of light. Tests of the stability of verdigris to heat and ultraviolet light have also been undertaken by Schweizer and Mühlethaler (1968).

Destructive Action on Paper

Verdigris, in common with other copper pigments, will degrade cellulosic materials and the phenomenon has now been well documented in a variety of different contexts (see Mairinger et al., 1980; Banik et al., 1982; Banik & Stachelberger, 1984). Severe damage to the fibers of works of art on paper probably results from the autocatalytic oxidation of cellulose by copper(II) ions, although the detailed mechanism of reaction has not so far been elucidated (Banik, 1982). Environmental conditions, in particular levels of illumination and atmospheric sulfur dioxide, play an important part in the deterioration of paper in contact with copper-containing green pigments (Banik & Ponahlo, 1983).

Microchemical Tests

Gettens and FitzHugh (see chapter 1) recommended methods for the microchemical detection of the presence of copper, in the form of copper ferrocyanide—Cu₂Fe(CN)₆ (Augusti, 1937); potassium copper lead hexanitrite—K₂PbCu(NO₂)₆ (Geilmann, 1954); or copper mercury rhodanide—Cu(CNS), Hg(CNS), H₂O (Short, 1940). The presence of the acetate group can be established with uranyl formate as sodium uranyl acetate—NaUO₂(CH₃COO)₃ (Hetterich, 1931). To carry out this test, a paint sample (about the size of a poppy seed c.100 γ) is boiled in a small pointed tube with some sodium carbonate solution, centrifuged, and then the supernatant liquid is removed with the aid of a capillary. Subsequently, the solution is evaporated on a slide, and—when cooled—a drop of the uranyl formate reagent is added. (The reagent is prepared by dissolving 10 g uranyl nitrate in 500 ml water, adding concentrated ammonia, and washing the resulting precipitate with small amounts of hot water. The precipitate is dissolved in pure formic acid and the solution is evaporated to dryness. One g uranyl formate is dissolved in 8 ml water, 1 ml formic acid is added and the solution is then filtered.) If acetate is present in the unknown test solution, pale yellow tetrahedra of sodium uranyl acetate are formed (see also Geilmann, 1954).

Spot Tests

A suitable test for the detection of copper is a slightly modified version of the procedure described by Feigl (1958), catalysis of the ferrothio-sulfate reaction by copper ions (limit of detection 0.02 µg Cu). The paint sample is decomposed on a white spot plate with one drop of hydrochloric acid (1:1 dilution). One drop of a 1.5% ferric chloride solution, and one drop of a 5% potassium thiocyanate (KCNS) solution is then added. To the dark red solution of ferric thiocyanate thus obtained, two drops of a 1.6% sodium thiosulfate solution (0.1 M) are added. If copper ions are present, the dark red solution is almost immediately decolorized. A sample that does not contain copper is only decolorized after one to two minutes.

A sensitive spot test for copper using rubeanic acid (dithio-oxamide) is described by Plesters (1956).

For the detection of the *acetate group*, a slightly modified version of the adsorption of iodine on basic lanthanum acetate—a not very sensitive

method described by Feigl (1956)—can be used. The paint sample is boiled with a 10% sodium carbonate solution and subsequently centrifuged. A drop of the clear supernatant solution is mixed on a white spot plate with three drops of a 15% lanthanum nitrate solution and three drops of a 0.13% (0.005 M) iodine solution. Next, a drop of a 1.7% (1 M) ammonia solution is added. If acetate is present, a blue–violet precipitate is formed after some time; in the case of small quantities of acetate, this is only visible under the microscope. The limit of detection is 50–60 µg of acetic acid.

Criteria for Certain Identification

In many cases, verdigris can only be recognized directly under the microscope (fig. 7). Typical characteristics are: the blue–green color, the particle morphology, and their pleochroism (see Particle Characteristics and Optical Properties).

The following are instrumental methods for the identification of verdigris.

Emission Spectrometric Analysis

This method is preferred at the Doerner Institute for the detection of the elements present in a paint sample. The identification of copper is based on the two very strong lines, at 3274.0 Å and 3247.5 Å, in the ultraviolet range. Analytical lines at 2824.4 and 2247.0 Å in the spark spectrum may also be used. The limit of detection lies at about 0.0001% (Waring & Annell, 1953). The advan-

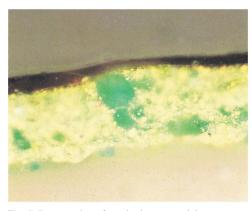
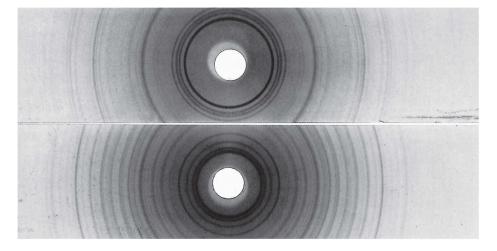


Fig. 7 Cross section of a paint layer containing verdigris. Lucas Cranach the Elder, c.1540, winged altarpiece of the *Passion of Christ*, Bayerische Staatsgemäldesammlungen (BSTG), Inv. No. 695. Reflected light, c. 328x.

tages of emission spectrum analysis as compared with microchemical analysis and spot tests are the higher sensitivity of this method and the possibility of detecting all the elements present in a sample at the same time. If the elements occurring in the paint sample are known, conclusions can often be drawn as to the mixture of pigments involved. For example, a copper-containing green paint that does not contain arsenic cannot comprise Scheele's green (copper arsenite) or emerald green (copper acetoarsenite).

Fig. 8 X-ray diffraction powder patterns for verdigris. A. Neutral verdigris Cu(CH,COO), H,O.

B. Blue basic verdigris (prepared at the Doerner Institute) [Cu(CH₃COO)₂]₂. Cu(OH)₂. 5H₂O.



B

Α

Table 2 Principal X-ray Diffraction Lines for Verdigris

Blue Basic Verdigris (prepared at the Doerner Institute) [Cu(CH ₃ COO) ₂] ₂ . Cu(OH) ₂ .5H ₂ O d(Å) I		Neutral V	erdigris/
		Cu(CH ₃ COO) ₂ .H ₂ O d(Å)	
8.19	6	6.91	10
4.11	7	6.17	4
2.40	5	5.87	3
2.16	3	5.38	3
2.03	5	3.59	1
1.71	5	3.53	2
		2.29	1

X-ray Diffraction Analysis

All the varieties of verdigris are crystalline and can therefore be detected by x-ray powder diffraction. Difficulties are encountered, however, when the paint sample contains, in addition, other pigments such as lead white and lead—tin yellow. X-ray powder diffraction patterns permit the distinction between different kinds of verdigris (fig. 8). The list in table 2 gives a selection of *d*-values, which can be used to distinguish between blue basic verdigris and neutral verdigris (see also table 3 for fuller data).

Strong diffraction lines for two other forms of basic copper acetate are given in Orna et al. (1985):

 $Cu(CH_3COO)_2$. $[Cu(OH)_2]_2$ at 2.39–2.33, 2.06–2.02, and 1.53–1.50 Å; $Cu(CH_3COO)_2$. $[Cu(OH)_2]_3$.2 H_2O at 9.76–9.11, 2.38–2.33, 2.05–2.02, and 1.41 Å.

Some of the closely spaced lines, particularly for the higher *d*-values, may only be resolved by the x-ray diffraction goniometer and not on a Debye-Scherrer pattern.

X-ray Spectrometric (X-ray Fluorescence) and Electron-Probe Microanalysis

The main lines for copper are the $K\alpha$ pair at c.8.0 keV and $K\beta$ at 8.9 keV (Birks, 1963).

Table 3 X-ray Diffraction Data for Verdigris

Verd [Cu(CH	Basic ligris 3COO) ₂] ₂ . ') ₂ .5H ₂ O	Blue Bo Verdign Cu(CH ₃ C Cu(OH) ₂ .	ris ^a (OO) ₂	Neutral Ver	
d(Å)	I	d(Å)	I	d(Å)	I
17.32	4	_	_	_	
12.27	7			_	_
11.94	8	_		_	_
9.31	10	0.40	_		
8.50	9	8.42	4		
8.19	6	_	_		
7.83	4	6.70	_	6.01	10
_		6.70	_	6.91	10 3.5
		5.83		6.17 5.87	2.5
_		3.63	_	5.75	1.6
				5.38	2.5
_		4.85	_	_	
4.48	5	_			_
	_			4.28	0.2
4.11	7	4.08	_	4.09	0.4
3.80	2	3.88	3		_
		3.56	_	3.59	1.2
_	_		_	3.53	2
		3.45	8	3.46	0.4
3.42	4	_		3.43	0.4
		3.31	7	3.29	0.4
3.21	2		_		_
3.06	5	3.10	9	3.09	0.4
		_	_	3.03	0.2
				2.97	0.2
_		2.83	5	2.77	0.2
_		2.73 2.64		2.72 2.65	0.2
			_	2.54	0.2
		2.48		2.34	
2.40	5			2.39	0.4
2.32	1			2.33	0.8
_			_	2.29	1
	_	2.21	6	2.23	0.4
2.16	3	2.11	10	2.14	0.2
	_	2.06	_	2.04	0.2
2.03	5	_		2.03	0.4
		1.86		_	
1.71	5 3	_		1.71	0.2
1.52	3	_		_	

a. Data from (Van't Hul-Ehrnreich & Hallebeek, 1972).

b. Data adapted from *JCPDS Powder Diffraction File* 27–145 and 27–145a (1977). (Courtesy of JCPDS International Centre for Diffraction Data.)

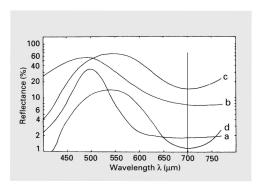


Fig. 9 Color reflectance curves for verdigris.

A. Neutral verdigris without medium,
Cu(CH₃COO)₂.H₂O. Maximum: 498 nm.
B. Blue basic verdigris without medium,
[Cu(CH₃COO)₂]₂.Cu(OH)₂.5H₂O. Maximum: 485 nm.
C. Copper resinate prepared according to
De Mayerne's recipe. Maximum 545 nm.
D. Commercially available copper resinate. Maximum: 537 nm.

Color and Spectral Reflectance

The maximum for the color-reflectance curve for neutral verdigris (Cu(CH₃COO)₂.H₂O) without binding medium lies at 498 nm; for basic verdigris ([Cu(CH₃COO)₂]₂.Cu(OH)₂.5H₂O) it is at 485 nm (fig. 9). For color-reflectance maxima of verdigris in various binding media, see General Pigment Properties.

Infrared Spectrophotometry

Figure 10 shows the infrared absorption curves for neutral verdigris (Cu(CH₃COO)₂.H₂O) and basic verdigris ([Cu(CH₃COO)₂]₂. Cu(OH)₂.5H₂O). As the composition of basic verdigris is variable, deviations from the infrared spectrum shown in figure 10B are likely. Verdigris can be detected in paint samples by means of infrared spectrophotometry (Kühn, 1964). A characteristic of verdigris is a band between 1560–1610 cm⁻¹, which is caused by a fundamental stretching vibration of the acetate group (figs. 10A and B, and 11). If a beam condenser and scale expansion of the ordinate are applied, 30–100 μg of paint sample would be sufficient for detection.

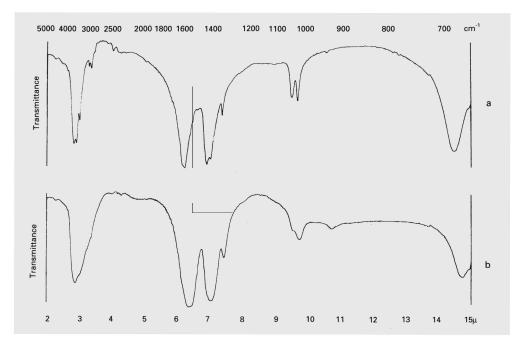


Fig. 10 Infrared spectra of verdigris without medium. NaCl prism, KBr micro-pellet technique.

A. Neutral verdigris, Cu(CH₃COO)₃, H₂O.

B. Blue basic verdigris, [Cu(CH₃COO)₂]₂.Cu(OH)₂.5H₂O.

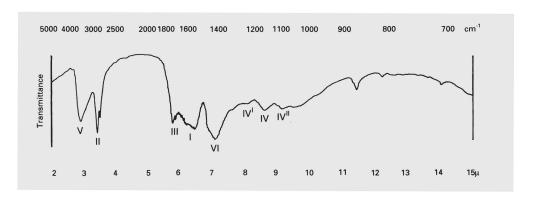


Fig. 11 Infrared spectra of a paint sample from *The Battle on the Issus River* by A. Altdorfer, BSTG, Munich, Inv. No. 688.

KBr micro-pellet, beam condenser, amount of paint sample 80 µg. Characteristic bands for:

Verdigris $6.20-6.4~\mu~(1610-1560~cm^{-1})~(I)$ Oil-medium $3.4~and~3.5~\mu~(2960~cm^{-1}~and~2850~cm^{-1})~(II)$ 5.75 and $5.83~\mu~(1740~cm^{-1}~and~1710~cm^{-1})~(III)$ 8.6 $~\mu~(1165~cm^{-1})~(IV)$ 8.08 $~\mu~(1250~cm^{-1})~(IV')$ 9.10 $~\mu~(1110~cm^{-1})~(IV'')$

The band at 2.9 μ (3450 cm⁻¹)(V) is due partly to verdigris, partly to the oxidized oil-medium. The band at c.7.1 μ (1410 cm⁻¹)(VI) can be ascribed both to verdigris, to the oil-medium, and to the lead white present in the sample.

The infrared spectrum of neutral verdigris has been examined in detail by Heyns (1972). Structurally, copper(II) acetate monohydrate consists of dimeric molecules in which the copper(II) ions are bridged in pairs by four acetate groups, with two water molecules occupying the terminal positions (Van Niekerk & Schoening, 1953). The principal infrared assignments give -CH3 vibrations at 2985, c.2935, 1445, 1356, 1053, and 1032 cm⁻¹, and the C-O symmetrical stretching band of the acetate groups at 1421 cm⁻¹, with the unsymmetrical stretching vibration occurring at 1605 cm⁻¹. A bending mode for -COO contributes an absorption at 691 cm⁻¹ (Heyns, 1972). The far infrared spectrum between 525 and 40 cm⁻¹ has been reported by Faniran and Patel (1974), while strong bands attributable to the coordinated water molecules at 3482 and 3378 cm⁻¹, with weaker features at 3278 and 1650 cm⁻¹, have been assigned by Baraldi and Fabbri (1981).

X-radiography

The mass absorption coefficient μ/ϱ of neutral verdigris at a wavelength of 0.708 Å is approximately 16.9, based on mass absorption coefficients of

Cu=51.0, C=0.6, O=1.22, and H=0.44 (Hodgman, 1960), and is thus lower than those of malachite (27.0) and azurite (26.0). Nevertheless, paint areas containing verdigris usually show strong x-ray absorption (little blackening of the film). The reason for this is the presence of strongly absorbing pigments such as lead—tin yellow and lead white in verdigris paints and in lead white paints beneath the verdigris.

Notable Occurrences

De Wild (1931) detected verdigris in nine Dutch paintings. Plesters (1956) identified verdigris in a painting by Memling. Roosen-Runge (1967) found verdigris in illuminated manuscripts from the early Middle Ages. At the Doerner Institute, the presence of verdigris has been established on eighty paintings and four polychrome sculptures, as shown in Notable Occurrences.

Notable Occurrences

Verdigris		Admixtures of Other
Date	Artist/Country, Title, Description, Collection or Location	Pigments and Method of Identification
1st quarter 13th C	German Christ Enthroned (reverse of a Shrine, the front depicting a Madonna with Child) Alte Kapelle, Regensburg	Lead white, Orpiment micr. + spectr. + IR-spectr.
c.1300	Giotto Last Supper BSTG, 643	Green earth, Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1350	Nardo di Cione Five Saints BSTG, WAF 1027	Lead white, micr. + spectr. + IR-spectr.
end 14th C	Bohemian The Annunciation Institut für Denkmalpflege, Dresden	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1400-1420	Conrad von Soest Saint Paul BSTG, WAF 459	Lead white, micr. + spectr.
c.1415	Master of the Bambino Vispo The Last Judgment BSTG, 10201	Lead-tin yellow, micr. + spectr.
c.1440	Fra Angelico da Fiesole The Martyrdom of Sts. Cosmas and Damian BSTG, WAF 38	Lead-tin yellow, micr. + spectr. + IR-spectr.
2nd quarter 15th C	Giovanni di Paolo di Grazia Birth of Saint John the Baptist BSTG, L884	Lead-tin yellow, micr. + spectr. + IR-spectr.
2nd quarter 15th C	Giovanni di Paolo di Grazia Saint John the Baptist before Herod BSTG, L885	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1450	German, Allgäu The Adoration of the Magi private collection, Munich	Lead-tin yellow, micr. + spectr.
c.1469	Master of the Schotten Altar, Schotten Altarpiece Scenes of the Passion Prelacy of the Schotten Foundation, Vienna	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1475	Master of the Schotten Altar, Schotten Altarpiece, Master of the St. Mary panels Scenes from Life of the Virgin Prelacy of the Schotten Foundation, Vienna	Lead-tin yellow, Lead white, micr. + spectr. + IR-spectr.
c.1470	Dieric Bouts the Elder Resurrection of Christ BSTG, 1449	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1483	Michael Pacher Altar of the Church Fathers BSTG, 2597–2600	Lead-tin yellow, Lead white, micr. + spectr.

BSTG = Bayerische Staatsgemäldesammlungen, Munich

micr. = Identification with the microscope

spectr. = Identification with the emission spectograph

IR-spectr. = Infrared spectroscopy

Date	Artist/Country, Title, Description, Collection or Location	Admixtures of Other Pigments and Method of Identification
4th quarter 15th C	Michael Pacher Altar of Saint Lawrence BSTG, 2592, 5304–5306	Lead white, micr. + spectr.
4th quarter 15th C	Francesco di Giorgio di Martino The Miracle of Saint Anthony and the Ass BSTG, 1020	—, micr. + spectr.
4th quarter 15th C	Francia The Virgin and Child with Two Angels BSTG, 1052	Lead white, micr. + spectr. + IR-spectr.
4th quarter 15th C	Piero di Cosimo Scene from the Legend of Prometheus BSTG, 8973	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1500	Gentile Bellini Portrait of a Young Man BSTG, WAF 1151	Green earth, micr. + spectr.
c.1500	Giovanni Battista, known as Cima da Conegliano The Virgin and Child with Saint Mary Magdalene and Saint Jerome BSTG, 992	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1500	German, Nuremberg The Parting of the Apostles BSTG, 1494	Lead-tin yellow, micr. + spectr. + IR-spectr.
c.1500	Giorgione Flute-playing Faun BSTG, 76	—, micr. + spectr. + IR-spectr.
c.1500	Style of Pasqualino Veneto Sacra Conversazione Parish Church, Pöbring, Lower Austria	Lead-tin yellow, Lead white, micr. + spectr. + IR-spectr.
c.1506	Raphael The Tempi Madonna BSTG, WAF 796	Lead white, micr. + spectr.
c.1510	Nikolaus Horverk, called Slesitzer Christ on the Mount of Olives BSTG, 1370	—, micr. + spectr. + IR-spectr.
c.1515	Leonhard Beck Altarpiece Hütten-chapel, Pflach near Reutte, Austria	Lead-tin yellow, micr. + spectr.
c.1515	Austrian Altarpiece Parish Church, Ossiach, Kärnten	Lead-tin yellow, Lead white, Vegetable black, micr. + spectr.
c.1515	Titian Vanity of the World BSTG, 483	Lead white, micr. + spectr. + IR-spectr.
c.1520	Titian Portrait of a Young Man BSTG, 517	Bone-black, Ochre. The verdigris forms part of a black paint (perhaps as a drying agent), micr. + spectr.
1548	Titian Emperor Charles V BSTG, 632	Vegetable black. The verdigris forms part of a black paint (perhaps as a drying agent), micr. + spectr.

Date	Artist/Country, Title, Description, Collection or Location	Admixtures of Other Pigments and Method of Identification
3rd quarter 16th C	Titian Christ Crowned with Thorns BSTG, 2272	Vegetable black, Ochre. The verdigris forms part of a black paint (perhaps as a drying agent), micr. + spectr.
c.1520	German, Allgäu Sippenaltar BSTG, 9692	Yellow ochre, micr. + spectr.
c.1520	German, Allgäu The "Helpers in Need," Egidius, Erasmus and Blasius BSTG, 9866	—, micr. + spectr.
1524	Hans Holbein the Younger Last Supper Kunstmuseum, Basel	Lead-tin yellow, micr. + spectr. + IR-spectr.
1st quarter 16th C	Francesco di Cristofano, called Franciabigio <i>Madonna and Child</i> BSTG, 8886	Lead-tin yellow, micr. + spectr. + IR-spectr.
1st quarter 16th C	Mathias Grünewald The Blessed Erasmus and Saint Maurice BSTG, 1044	1) As a glaze on gold 2) As an addition to a black color prepared from a vegetable black (perhaps a drying agent), micr. + spectr. + IR- spectr.
1st quarter 16th C	Giovanni Antonio Bazzi, called Sodoma The Holy Family BSTG, WAF 1025	—, micr. + spectr. + IR-spectr.
c.1520–1530	Giovanni Antonio Sogliani Madonna and Child with the Infant John the Baptist Royal Family, Denmark	Lead white, Lead-tin yellow, Ochre, micr. + spectr.
1529	Albrecht Altdorfer The Battle on the Issus River (Alexanderschlacht) BSTG, 688	Lead white, micr. + spectr. + IR-spectr.
c.1540	Lucas Cranach the Elder Passion of Christ BSTG, 12989	Lead white, Lead-tin yellow, micr. + spectr. + IR-spectr.
1542	Marinus van Roymerswaele <i>A Notary</i> BSTG, 718	Lead-tin yellow, micr. + spectr.
1546	Monogrammist AE Peter Canisius BSTG, WAF 170	—, micr. + spectr. + IR-spectr.
2nd quarter 16th C	Bartholomäus Bruyn the Elder Portrait of a Man Landesgalerie, Hanover KM 1920/38a	—, micr. + spectr.
2nd quarter 16th C	Bartholomäus Bruyn the Elder Virgin and Child BSTG, WAF 155	Lead-tin yellow, Ochre, micr. + spectr. + IR- spectr.
2nd quarter 16th C	Sebastiano del Piombo Half-length Portrait of a Priest BSTG, 1300	Ochre, micr. + spectr. + IR-spectr.

Date	Artist/Country, Title, Description, Collection or Location	Admixtures of Other Pigments and Method of Identification
2nd–3rd quarter 16th C	Girolamo Mazzola-Bedoli Virgin and Child with Saint Bruno BSTG, 5289	Green earth, micr. + spectr.
c.1550	Netherlandish Landscape BSTG, 9893	Lead-tin yellow, micr. + spectr. + IR-spectr.
1572	Lucas Cranach the Younger Elector August and His Family before the Crucifixion Altarpiece in the Chapel of Castle Augustusburg/Erzgebirge	—, micr. + spectr. + IR-spectr.
2nd quarter 16th C	Tintoretto Mars and Venus Surprised by Vulcan BSTG, 9257	Lead white, micr. + spectr.
1570–1580	Tintoretto Christ in the House of Mary Magdalene and Martha BSTG, 4788	Lead white, micr. + spectr.
before 1579	Tintoretto Gonzaga Cycle, 1st row: The Emperor Creating Gianfranco Gonzaga First Marquis of Mantua BSTG, 7303	Lead-tin yellow, Ochre
	The Battle of Legnano BSTG, 7304	Azurite, Lead white, Yellow lake pigment
	The Battle on the Taro BSTG, 7309	Ochre, Lead-tin yellow, micr. + spectr.
1579–1580	Tintoretto Gonzaga Cycle from Mantua, 2nd row: <i>The Capture of Parma</i> BSTG, 7306	Orpiment, Realgar
	The Capture of Pavia BSTG, 7308	Azurite, Lead white, Ochre, Lead-tin yellow micr. + spectr.
2nd half 16th C	Stephan Maier Legend of Saint Magnus BSTG, 9859	Azurite (over the azurite lies a brownish yellow glaze which contains single crystals of verdigris), micr. + spectr. + IR-spectr.
between 1601–1605	Johann Georg Fischer Duke Ludwig of Bavaria Triumphs Near Mühldorf BSTG, 3743	Vegetable black. The verdigris here is an addition to a black paint (perhaps as a drying agent), micr. + spectr.
between 1601-1605	Johann Georg Fischer Duke Ludwig IV of Bavaria Elected King of the Romans BSTG, 3745	Vegetable black, Smalt, Ochre, micr. + spectr.

Date	Artist/Country, Title, Description, Collection or Location	Admixtures of Other Pigments and Method of Identification
between 1601–1605 Johann Georg Fischer The Battle at Ampfing BSTG, 3750		Vegetable black, Lead-tin yellow. The verdigris here is an addition to a greenish-black paint (perhaps as a drying agent). micr. + spectr.
c.1610	Abraham Janssens van Nuyssen <i>Phoebe with Her Nymphs</i> BSTG, 13111	Lead-tin yellow, micr. + spectr.
2nd decade 17th C	Abraham Janssens van Nuyssen Mount Olympus BSTG, 4884	Lead-tin yellow, micr. + spectr.
1615–1616	Peter Paul Rubens Martyrdom of Saint Lawrence BSTG, 338	Lead-tin yellow, micr. + spectr.
c.1620	Peter Paul Rubens Fall of the Damned into Hell BSTG, 320	Lead-tin yellow, Lead white, micr. + spectr. + IR-spectr.
1622–1625	Peter Paul Rubens Sketches for the Medici-Cycle: <i>The Marriage</i> of the Princess BSTG, 94	Single crystals of verdigris in brown glazing paint, micr. + spectr.
c.1624	Cornelis de Vos Portrait of a Woman BSTG, 6303	Lead-tin yellow, micr. + spectr.
c.1624	Cornelis de Vos Portrait of a Man BSTG, 6306	Lead-tin yellow, micr. + spectr.
1st quarter 17th C	Domenichino Saint Matthew and the Angel BSTG, 1017	Constituent of a black paint, which contains vegetable black (perhaps as a drying agent), micr. + spectr.
1st quarter 17th C	Sebastian Vrancx The Surprise Attack BSTG, 6295	Lead-tin yellow, Ochre, micr. + spectr.
2nd quarter 17th C	Frans Francken the Younger, Virtue and Vice BSTG, 860	Lead-tin yellow, micr. + spectr.
2nd quarter 17th C	Johann Ulrich Loth The Judgement of Solomon BSTG, 2566	Ochre, micr. + spectr.
2nd quarter 17th C	Johann Ulrich Loth Doubting Thomas BSTG, 5154	—, micr. + spectr.
2nd quarter 17th C	Johann Ulrich Loth The Holy Family BSTG, 7373	—, micr. + spectr. + IR-spectr.
1653	Abraham Hendricksz. van Beyeren Large Still Life with Crawfish BSTG, 1620	Lead white, Ochre, micr. + spectr.
c.1660	Jan Vermeer The Girl with the Pearl Earring Mauritshuis, Hague	Vegetable black, Ochre, Lead white. The verdigris is a component of a brown paint. micr. + spectr.

Date	Artist/Country, Title, Description, Collection or Location	Admixtures of Other Pigments and Method of Identification
3rd quarter 17th C	Abraham Mignon Still Life with Fruit BSTG, 6427	—, micr. + spectr.
1678	Eglon Hendrik van der Neer Lady Tuning a Lute BSTG, 204	—, micr. + spectr. + IR-spectr.
c.1688	Franz Werner Tamm Still Life with Doves BSTG, 1670	Green earth, micr. + spectr.
2nd half 17th C	Melchior d'Hondecoeter Fowls BSTG, 401	Lead white, Ochre, micr. + spectr.
4th quarter 17th C	Claudio Coello Saint Peter of Alcantara BSTG, 471	Lead white, micr. + spectr.
1715	Herman van der Mijn Garden Flowers BSTG, 904	Green earth, micr. + spectr.
2nd quarter 18th C	Caspar Hirschel Still Life BSTG, 5958	Green earth, micr. + spectr.
2nd–3rd quarter 19th C	Barend Carnelis Koekkoek Rocky Landscape with Chapel BSTG, 12904	Ochre, micr. + spectr.
1874	August Wolf (copy after Veronese) The Marriage of Saint Catherine BSTG, 11691	Lead white, Green earth, micr. + spectr.
c.1877	Ernst von Liphart (copy after Titian) Allegory of Alfonso Davalos BSTG, 11685	Lead white, micr. + spectr.
Verdigris on Polychro		
c.1230	German Group: <i>Triumph of the Cross</i> Cathedral of St. Mary at Freiberg, Saxony	Lead white, micr. + spectr. + IR-spectr.
1220–1240	German Madonna and Child Ruhpolding, Bavaria	1) Verdigris as a glaze over a paint layer consisting of Green earth and Lead white 2) Green earth, Lead white 3) Green earth, Smalt, micr. + spectr. + IR-spectr.
1484–1489	Bernt Notke Statue of Saint George Stockholm	 Lead-tin yellow, Lead white, Ochre Ochre, Lead white Lead-tin yellow, micr. spectr. + IR-spectr.
1497	Michael or Gregor Erhard Moerlin-Memorial Schatzler Palace, Augsburg	Verdigris crystals in a yellowish brown glazing paint, micr. + spectr. + IR-spectr.

B. Copper Resinate (Transparent Copper Green)

Copper resinate is the name commonly given to the transparent green glazes that are colored by copper salts of resin acids.

History of Use

There is some uncertainty as to the extent to which copper resinate was used in various periods of painting. It is true that on various occasions green copper-containing glazing paints have been found that do not show discrete pigment particles on examination under the microscope, but this alone does not unambiguously prove the presence of copper resinate. Laurie (1914), for example, reported the occurrence of a grass-green, transparent copper-containing pigment in illuminated manuscripts from the eighth to the fourteenth centuries. On the basis of the brittleness of these paint layers and the nature of the fracture, Laurie assumed that the compound in question is a resinlike compound, and is, therefore, copper resinate. Flieder (1968) found similar transparent copper greens in fifteen specimens from illuminated manuscripts of the tenth to fifteenth centuries and identified these as copper-protein compounds. Flieder pointed out that these compounds may have formed in the course of time as a result of a reaction of verdigris or malachite with the protein medium or with the proteins of the parchment. Roosen-Runge (1967) also found on illuminated manuscripts from the early Middle Ages, glassy green paint that shows discrete particles of verdigris. So far, no positive proof has been found that copper resinate was used in manuscript illumination.

A transparent, copper-containing green paint has similarly been noted on many Early Netherlandish and Early Italian paintings (Coremans et al., 1952–1954; Coremans et al., 1959; Coremans & Thissen, 1961; Ruhemann, 1955–1956; Sneyers & Thissen, 1958; Thissen & Vynckier, 1964). This paint often shows a brown discoloration at the surface. It is assumed that copper resinate was used in these paintings, but this suggestion is based only on microscopic observations and the positive test for copper. A number of such instances are listed for pictures in the National Gallery, London (see Notable Occurrences). Resin acids were not generally sought.

It appears that this glazing pigment was most commonly used for Italian easel paintings in oil in the sixteenth century and in Northern painting in the fifteenth and sixteenth centuries, although earlier and later occurrences have also been noted, including some from nineteenth-century paintings. It seems not to be a usual feature of the palette anywhere in Europe after the end of the sixteenth century despite the best-known surviving recipe from the De Mayerne manuscript dating from the seventeenth century, perhaps because the tendency to discolor was already widely appreciated by this time. Where analyses have been carried out, the usual medium for copper resinate is one of the drying oils (see for example, Mills & White, 1981; 1983; and 1985), and in at least one case it has been established that a copper resinate layer on a small panel by Raphael was bound in walnut oil, while the remainder of the picture proved to be egg tempera (Mills & White, 1985).

It is perhaps to be expected that where tempera panels contain translucent greens, for example to embellish gold leaf, the binding medium for the glaze is likely to be oil, in keeping with the suggestion by Cennino Cennini that verdigris should be ground in a drying oil for the same purpose. It is also probable that the oil would have been added during the preparation of the pigment, as some of the early recipes imply. It should be mentioned, however, that verdigris in oil-media without the addition of other pigments has a very pronounced glazing effect, and that the outlines of crystals of verdigris are often very difficult to recognize under the microscope. In addition, copper acetates (verdigris) react in the course of time with oilmedia to form transparent copper salts of fatty acids (Kühn, 1964; Mills, 1966). Copper acetates also react with proteinaceous media or resins to form transparent copper-protein compounds or copper salts of resin acids.

Up to the present time, the author, using infrared spectrophotometry, has only positively identified copper resinate in three paintings, although several examples of the detection of a component of pine resin has been reported for copper green glazes by the laboratory of the National Gallery in London using mass spectrometry (see Notable Occurrences).

Preparation

The best known early recipe for the preparation of copper resinate dates from the seventeenth century and is given by De Mayerne (Van de Graaf, 1958). According to this recipe, a "beautiful green," which owes its color to copper salts of resin acids, is obtained in the following manner:

Beau Verd. Rp. Therebentine de Venisse 3ij, huile de Therebentine 3jss. meslés, adjoustés. Vert de gris mis en morceaulx 3ij, mettés sur cendres chaude & faittes bouillir doulcement. Essayés sur vn verre si la couleur vous plaist; passés par vn ligne. [Beautiful Green. Recipe. Mix 2 ounces Venice turpentine and 1½ ounces turpentine, add 2 ounces verdigris in pieces, put on hot ash and let gently boil. Try on a glass, whether the color is pleasing to you; filter through a linen cloth.]

In this way a highly viscous, transparent mass is formed, which dries in a thin layer over the course of months and can then be pulverized, or it may have been used directly for glazing. The copper resinate is composed of copper salts of resin acids and colophony. De Mayerne also records a method for making "Vernix verd comme Esmeraude," involving heating verdigris and a yellow

lake pigment (Scudegrun or Schitgeel) with linseed oil, pine resin (Vernix de Therebentine), and oil of turpentine (Van de Graaf, 1958).

An earlier Florentine book dealing with painting (Birelli, 1601) includes a "method for making a green to put on glass instead of blinds," clearly referring to a copper resinate type glaze:

Take one pound of fine white turpentine resin [pine resin], three ounces of mastic . . . and half an ounce of new wax. Put everything together in a small newly-glazed pot, and boil the aforesaid things on a moderate fire of charcoal, mixing it all the time with a delicate little stick, until it no longer squeaks. This done, take it off the fire and strain it into another little glazed jar . . . Then add to these things an ounce of verdigris and put it in little by little, mixing it all the time in the jar with a little stick so that it is well incorporated . . . Return the little jar to the warm ashes, with the things in it nice and hot, and take your [piece of] glass, to which with a brush you apply the color using the above composition while it is still hot. (Translation by Joyce Plesters.)

The technique goes on to describe re-warming the copper resinate glaze over a fire to allow it to flow again, thus enabling a thin, even coat to be formed on the glass, and also a method of lightening the color by combining ground turmeric with the preparation.

This recipe does not call for the addition of drying oil such as would be incorporated into the glaze for painting, but the same author describes a second technique "to make green like the emerald" which starts with linseed oil, rock alum, and good quality verdigris, with the subsequent addition of pine resin (Birelli, 1601). Armenini (1586), writing somewhat earlier, also described the glazing of green draperies with verdigris in vernice comune, by which is probably meant pine rosin dissolved in linseed oil. Evidently, by the early nineteenth century these transparent greens were understood to be oil "varnishes" colored green by the addition of verdigris with heating. For example, The Painter and Varnisher's Guide gives a method for preparing a transparent green by combining copal varnish (implying the addition of a drying oil) with "crystallized verdigris" over a bain-marie (Tingry, 1816). While Marcucci (1813), writing at the beginning of the nineteenth century and speculating on how the Old Masters would have painted their draperies, described the final treatment of green underpaints which are:

then . . . glazed with distilled verdigris [verde eterno, that is, purified neutral verdigris], well ground, with one part of walnut oil, two of turpentine distillate, and one of pine resin [probably liquid rosin or balsam from Pinus picea], or Strassburg turpentine . . .

Currently, copper resinate is prepared by reacting a copper salt solution with an aqueous solution of sodium resinate or by melting resins with reactive copper salts (copper acetate, copper hydroxide, copper oxide, copper carbonate) (Masschelein-Kleiner, 1963).

Composition and Chemical Properties

Copper resinate is composed mainly of the copper salts of resin acids. If resins from conifers are used for its preparation, such as Venice turpentine (De Mayerne), copper salts of abietic acid (C₁₉H₂₉COOH) are formed as the main product. Abietic, dehydroabietic, pimaric, isopimaric, and sandaracopimaric acids are components of colophony, which is the residue from turpentine distillation (Mills & White, 1977). Copper resinate prepared from Venice turpentine or pine resin is decolorized by hydrochloric acid and caustic soda. It melts on heating and turns brown; if heated over a longer period and at higher temperatures, it decomposes to black copper oxide and carbon. Copper resinate is soluble in numerous organic solvents, such as benzene, chloroform, mineral spirits, and so on, but is insoluble when locked in a dried oil film. The solubility of pure samples subjected to artificial aging processes is practically unaffected.

Particle Characteristics and Optical Properties

Copper resinate prepared according to De Mayerne's recipe appears under the microscope as glassy, irregular, green fragments (fig. 12), with a refractive index of about 1.52.

Copper resinate found on paintings shows similar characteristics (fig. 13). Copper resinate has a neutral green color (fig. 14). The resinate prepared according to De Mayerne (maximum of the color reflectance curve: 545 nm, see fig. 9) is somewhat "warmer" in color than commercial copper resinate (maximum of the color reflectance curve: 537 nm).

Permanence

Prepared specimens of copper resinate without medium and in linseed oil, egg tempera, and gum arabic, were exposed under normal climatic conditions (55% RH, 20°C) to high-intensity shortwave ultraviolet radiation, to light from xenon lamps, and to fluorescent tubes as well as to day-

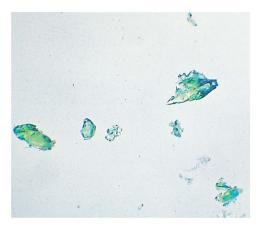


Fig. 12 Photomicrograph of copper resinate prepared at the Doerner Institute according to De Mayerne's recipe (1620). Transmitted light, c. 351x.



Fig. 13 Photomicrograph of fragments of copper resinate from a painting by Vermeer, *Maid Handing a Letter to Her Mistress*, Frick Collection, New York. Transmitted light, c. 320x.

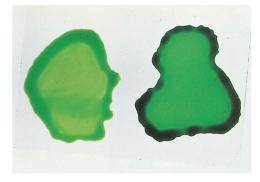


Fig. 14 Copper resinate. *Left*: prepared at the Doerner Institute according to De Mayerne's recipe (1620). (Maximum of the color reflectance curve: 545 nm.) *Right*: commercially available copper resinate. (Maximum of the color reflectance curve: 537 nm.)

light. In the last three cases, the exposure was equivalent to 120, 60, and 5 years, respectively, under usual lighting conditions. A brown discoloration occurred only under the high-intensity short-wave ultraviolet radiation (the same result was found in tests at the National Gallery, London), but exposure to daylight and to other light sources caused fading to a greater or lesser extent. This differing behavior of copper resinate is presumably because the oxidation of the resin acids proceeds differently under ultraviolet light when compared with the process under visible light (Schuller et al., 1962).

As already noted (Verdigris, Permanence and Compatibility with Other Pigments), a phenomenon often encountered in paintings is that areas originally green in color display a brown discoloration at the surface. This color change is frequently noted to be significantly less in areas hidden by the frame than in the body of the painting that is exposed to the light, and also that beneath the protective film of discoloration, unchanged green often persists (see, for example, fig. 15). Presumably the cause of this discoloration is the decomposition of copper resinate glazes under the influence of ultraviolet light. No conclusive proof has yet been obtained, however, that copper resinate glazes are generally involved in these cases. In addition, the slight indoor occurrence of shortwave ultraviolet radiation might not be sufficient, even over a period of several centuries, to cause the strong brown discoloration of copper resinate. This phenomenon is being investigated further at the Doerner Institute.

Translucent brown layers present at the surface of copper resinate glazes have been examined by Kockaert (1979) by means of thin paint cross sections and by fluorescence microscopy. The work concludes that embrownment is most often due to discoloration of copper resinate by an unknown photocatalytic reaction, although in some cases later paint, darkened varnish, or the presence of original colors applied to modify the hue of the green glaze may be responsible. The same author has published a thin section from a Crucifixion by Albert Bouts that shows the typical orange-brown color by transmitted light of an entirely discolored copper green glaze (see Goetghebeur & Kockaert, 1980-1981). The process of color change is presumed to involve photo-oxidation of the organic components of the paint film accompanied by reduction of the copper species perhaps to copper(I), but no experimental evidence for this mechanism has so far been obtained.

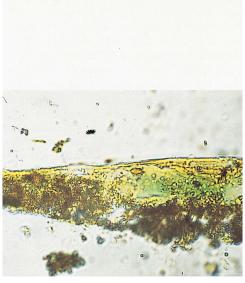
By using wavelength-dispersive x-ray microanalysis in the scanning electron microscope (SEM), Groen (1975) has been able to demonstrate the relatively homogenous distribution of copper in both brown and green portions of a copper resinate glaze showing surface discoloration, for samples from a painting by Lucas van Leiden dated 1526. More recently, Plesters et al. (1982) have obtained a similar result by energydispersive x-ray microanalysis applied to cross sections from a canvas painting by Veronese, in which both extensively browned and relatively unchanged true copper resinate glazes are present (see fig. 15).

Criteria for Certain Identification

The copper content of green transparent paints, which do not show discrete pigment particles under the microscope, is not positive proof of the presence of copper resinate. Suitable techniques for the determination of resin acids are thin-layer chromatography (Kléber & Masschelein-Kleiner, 1964) and gas chromatography (Masschelein-Kleiner et al., 1968). Gas chromatography, however, requires paint samples of about 1 mg, which can only rarely be taken from paintings. The most convincing method of identification is gas chromatography-mass spectrometry by which means the relatively stable dehydroabietate component of resinate films (Mills & White, 1977) may be detected by extracting the free acid and forming the methyl ester to be identified by its mass spectrum (Mills & White, 1981 and 1982; Dunkerton & Roy, 1986). Copper resinate can also be determined with the aid of infrared spectrometry (Kühn, 1964; Kléber & Masschelein-Kleiner, 1964). For the infrared spectrum, a paint sample of 0.1 mg is sufficient; this sample is pressed into a micro-pellet together with potassium bromide. The spectra of copper resinate samples given in figure 16 all show a band at approximately 1600 cm⁻¹, which can be ascribed to ionized carboxyl groups (-COO-). However, the fact that verdigris, as a copper salt of acetic acid, also produces a band between 1615-1560 cm⁻¹ should not be overlooked. Consequently, copper resinate occurring in mixtures with verdigris cannot be detected unambiguously by infrared spectroscopy alone. In addition, copper salts of fatty acids, which are formed in paint layers containing verdigris and oil-media, also show a band at approximately 1600 cm⁻¹ in the infrared spectrum (Mills, 1966).



Fig. 15 Examples of copper resinate use in paintings. A. Detail from Francia's *Portrait of Bartolomeo Bianchini*. National Gallery, London, No. 2487. Reproduced by permission of the Trustees.



B. Thin cross section of darkened foliage paint from the tree, left-hand edge in Francia's *Portrait of Bartolomeo Bianchini*. Note the brown discoloration of the green copper resinate glaze at the surface of the paint film, with unchanged green surviving beneath. The layer passes directly over sky paint containing lead white and ultramarine which is sufficiently opaque to appear dark in a thin section by transmitted light. 1,075x.



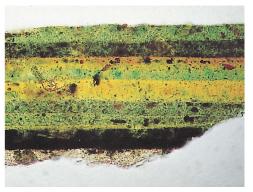
C. Detail from Veronese's *Allegory of Love, III* ("Respect"), showing the junction of a green drapery and brown brocade pattern, both finished with copper resinate glazes. Note the uneven discoloration between the two areas. National Gallery, London, No. 1325. Reproduced by permission of the Trustees.



D. Thin cross section from the brown, discolored copper resinate brocade pattern in Veronese's *Allegory of Love, III*. As in the case of the glaze in the Francia (B), unchanged green glaze is present beneath the surface. Transmitted light, 1,075x.



E. Paint cross section from deep green drapery in Cima's *The Incredulity of Saint Thomas*. National Gallery, London, No. 816. In common with other Venetian paintings, multilayered paint systems containing copper resinate glazes are used for strongly colored, saturated greens. The structure is more clearly evident in thin cross section (see F). Reflected light, 538x.



F. The same sample as in E shown as a thin cross section in transmitted light. Many layers of copper resinate green combined with other pigments are employed. Transmitted light, 538x.

All photomicrographs by A. Roy.

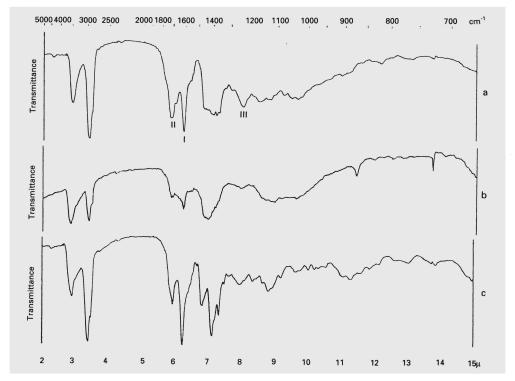


Fig. 16 Infrared spectrogram of copper resinate. KBr micro-pellet.

A. Prepared at the Doerner Institute according to De Mayerne's recipe. The band I at 6.2–6.25 μ (1610 cm $^{-1}$ –1600 cm $^{-1}$) can be ascribed to ionized carboxyl groups, that is to the copper salts of resin acids. The bands II at 5.83 μ (1710 cm $^{-1}$) and III at 8.05 μ (1240 cm $^{-1}$) are due to carboxylic acids as well as to

resin acids. Characteristic of resin acids is the band at $8.05~\mu~(1240~cm^{-1}).$

B. Copper resinate from a painting by Vermeer, *Maid Handing a Letter to Her Mistress*, Frick Collection, New York. Micro-pellet (about 100 µg of paint sample).

C. Commercially available copper resinate.

Notable Occurrences

Copper Resinate

Date	Artist/Country, Title, Description, Collection or Location	Remarks/Admixtures of Other Pigments and Method of Identification
c.1670	Jan Vermeer Maid Handing a Letter to Her Mistress Frick Collection, New York	The copper resinate layer is situated beneath a blue paint layer of lead white and ultramarine, micr. + spectr. + IR-spectr.
c.1725	German Polychrome stucco, Castle "Favorite" near Rastatt, Germany	The copper resinate occurs as a glaze on top of a layer of yellow ochre, micr. + spectr. + IR-spectr.
1873	Arnold Böcklin <i>Triton and Nereide</i> BSTG, 11534	The copper resinate is part of a sample which also contains cobalt blue and zinc white, micr. + spectr. + IR-spectr.

micr. = Identification with the microscope

spectr. = Identification with the emission spectograph

IR-spectr. = Infrared spectroscopy

Copper Resinate in Paintings in the National Gallery, London^a

Date	Artist	Title and Number
mid-late 1460s	Giovanni Bellini	The Agony in the Garden 726
15th C	Dieric Bouts	The Virgin and Child 2595
late 15th C	Studio of Hans Memling	The Virgin and Child 709
15th C	Antonio Pollaiuolo	Apollo and Daphne 928
late 15th C(?)	Style of Martin Schongauer	The Virgin and Child in a Garden 723
late 15th/early 16th C	Francia	Bartolomeo Bianchini 2487
1500	Sandro Botticelli	Mystic Nativity 1034
1504	Cima ^b	The Incredulity of St. Thomas 816
1503	Raphael ^b	The Crucifixion 3943
1505	Raphael	St. John the Baptist Preaching 6480
1511/1512	Raphael	Pope Julius II 27
c.1510(?)	Andrea Busati	The Entombment 3084
c.1509(?)	Gerard David	Virgin and Child with Saints and Donor 1432

a. Table compiled by A. Roy. The majority of occurrences were deduced from microscopical examination of paint cross sections and the detection of copper either by microchemical tests or spectrographic analysis with the laser microprobe. Drying oil was found in many of the green glaze samples by gas chromatography.

b. Resin components of the paint film confirmed by gas chromatography-mass spectrometry. See, for Cima, Dunkerton and Roy (1986); Raphael (Mills & White, 1985); Veronese (Mills & White, 1982; Mills & White, 1983).

Date	Artist	Title and Number
early 16th C	Gerard David	The Deposition 1078
early 16th C	Gerard David	The Adoration of the Kings 1079
between 1500-1515	Jan Gossaert	The Adoration of the Kings 2790
early 16th C(?)	Imitator of Robert Campin	The Death of the Virgin 658
early 16th C	Perugino	St. Raphael 288
1517(?)	Benvenuto Tisi, called Garofalo	Madonna and Child with Saints 671
c.1515–1516(?)	Palma Vecchio	Portrait of a Poet 636
c.1520	Palma Vecchio	A Blonde Woman 3939
1520	Albrecht Altdorfer	Christ Taking Leave of His Mother 6463
1523	Titian	Bacchus and Ariadne 35
1520s	Dosso Dossi	A Man Embracing a Woman 1234
c.1520s(?)	Lorenzo Lotto	Virgin and Child with Saints 2281
c.1530s(?)	Lorenzo Lotto	The Prothonotary Apostolic, Giovanni Giuliano 1105
1540s	Florentine School	Portrait of a Boy 649
1546	Bartolomeo Veneto	Portrait of Ludovico Martinengo 287
1543–1544	Tintoretto	Jupiter and Semele 1476
c.1556	Tintoretto	Christ Washing His Disciples' Feet 1130
1560	Tintoretto	St. George and the Dragon 16
c.1578	Tintoretto	The Origin of the Milky Way 1313
mid-16th C	Paris Bordon	Daphnis and Chloe 637
mid-16th C	Jacopo da Bassano	The Good Samaritan 277
mid-16th C	Pieter Bruegel the Elder	The Adoration of the Kings 3556
1570s(?)	Paolo Veronese	The Family of Darius before Alexander 294
late 16th C	Paolo Veronese ^b	Allegory of Love, II 1324
late 16th C	Paolo Veronese	Allegory of Love, III 1325
late 16th C	Paolo Veronese ^b	Allegory of Love, IV 1326
late 16th C	Studio of El Greco	St. Jerome as Cardinal 1122

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7

Vermilion and Cinnabar

RUTHERFORD J. GETTENS, ROBERT L. FELLER, and W. T. CHASE

Current Terminology

English: vermilion (cinnabar)
German: Vermilion, (m.) (Zinnober)
Spanish: vermellon, (m.) (cinabrio)
French: vermillon, (m.) (cinabre)
Italian: vermiglio, (m.) (cinabro)
Japanese: shu and shinsha

Chinese: tan-sha

Vermilion is the standard name in England and the United States given to the red artists' pigment based on artificially made mercuric sulfide. The mineralogist and crystallographer have given the common red crystalline form of mercuric sulfide the name *cinnabar*, which is reserved for the natural mineral and its specific crystal structure.

There are three kinds of mercuric sulfide pigment: (1) the natural mineral form, which is simply finely ground cinnabar; (2) a synthetic form, made by the dry-process, commonly called vermilion; and (3) a synthetic form, made by a wet-process, also called vermilion. The artificial products are derived indirectly from native cinnabar.

Obsolete Terminology and Synonyms

On the origin of the terms cinnabar and vermilion, we can quote Church (1890) who said,

Vermilion was formerly known as vermiculus, cinnabaris, cenobrium, and minium; the last name is now appropriated to red lead. Vermilion and vermiculus are de-

ROBERT L. FELLER, director emeritus, Research Center on the Materials of the Artist and Conservator, Carnegie-Mellon Research Institute, Pittsburgh. rived from the Latin vermes, a name originally designating the kermes insect found in the ilex or evergreen oak and used for the preparation of a red dye. From kermes, in its turn, the words crimson and carmine are derived. The name cinnabar is supposed to be of Indian origin, and was sometimes used to designate dragon's blood, a red resin. Theophrastus informs us that two kinds of cinnabar were known to the Greeks. One of these was undoubtedly real cinnabar (chiefly from Spain), the other was red lead. Pliny's cinnabar or minium was true vermilion; so was the minium of Vitruvius. Theophilus called it cenobrium.

Harley (1982) wrote, "In English two names, cinnabar and vermilion, have been used interchangeably in the past to describe either the natural or the manufactured product, but, by the seventeeenth century, vermilion was used more frequently." Thus, the confusion of ancient terminology when applied to pigments is well exemplified by vermilion.

Sources of Cinnabar and Mercury

Cinnabar, a dense red mineral, is the principal ore of the metal mercury or quicksilver; it is found fairly widely, but not abundantly, distributed in the world. It is mentioned by the fourth-century Greek writer, Theophrastus, the author of *De Lapidibus*, but Caley and Richards (1956), the translators, indicated that cinnabar was known in Greece as early as the sixth century B.C. and perhaps in Asia Minor long before that.

Strangely, cinnabar was not used in Dynastic Egypt or in the early civilizations of Mesopotamia. It was not mentioned by Lucas in his Ancient Egyptian Materials and Industries.

Cinnabar was well known to the Romans, and according to Pliny (Bailey, 1929) almost the entire Roman supply came from Sisapu (or Sisopo) in

Spain. The reference is probably to the famous mines of Almaden, which are still the most important source of mercury in the world. In addition to sources in Spain, Dana (Palache et al., 1952) indicated there are deposits in Asia, in the Altai, and in the Ferghana region of Russian Turkestan, which have been worked for quicksilver for a thousand years. In China it occurs in the provinces of Kweichow and Hunan, at times as large twinned crystals in drusy quartz. Brelich (1904-1905) described in detail primitive methods of mining cinnabar at the turn of this century in the province of Kweichow and the production of quicksilver from it in iron and clay retorts. The quicksilver was exported to different parts of China "where it is used for the manufacture of vermilion, for which there is great demand throughout the Chinese Empire." There are sources in Russia, Yugoslavia, Germany, and Italy. In the New World there are deposits in Peru, Mexico, Texas, and California. Cinnabar is often associated in nature with elemental mercury, with heavy metal sulfides such as pyrite, marcasite, and stibnite, and often in a gangue of opal, chalcedony, quartz, gypsum, calcite, and dolomite (fig. 1) and, less frequently, with fluorite and barite. In the Almaden deposits it occurs as a replacement of the quartzites interbedded with bituminous shale associated with sericite, pyrite, and azeolite. In many deposits, cinnabar occurs in veins and impregnations near recent volcanic rocks and hotspring deposits.

The metal mercury is prepared from lump cinnabar ore by combined roasting and distillation. Air supplies oxygen for the reaction: $HgS + O_2 \rightarrow Hg + SO_2$. The mercury vapor is condensed in brick or cement chambers.

Preparation

Ground Cinnabar

The red ore was probably broken into small pieces and further reduced by grinding in a stone mortar. The Roman architect Vitruvius (Morgan, 1926), writing in the first century A.D., said, "When the lumps of ore are dry, they are crushed in iron mortars and repeatedly washed and heated until impurities are gone and the colours come . . ." He went on to mention the use of cinnabar in coloring the polished stucco finish of interior walls, where it is stable only if not exposed to the sun. Augusti (1967), however, reported only one specimen of ground cinnabar among the many specimens of



Fig. 1 Native cinnabar (mercuric sulfide) associated with calcite from Terlingua, Texas. Courtesy Smithsonian Institution, Department of Mineral Sciences, specimen 53695. Slightly reduced from natural size.

Roman pigments from Pompeii which he examined in the National Museum in Naples.

It is difficult to say how long or to what extent vermilion from ground cinnabar was used in Europe and whether it was used simultaneously with synthetic vermilion. Eibner (1917–1918) stated that cinnabar disappeared from artists' supply houses about 1880.

In China, according to Chêng Tê-k'un (1960 and 1963), cinnabar was used in Shang and Chou times for strewing in grave burials, presumably to preserve the bodies of the dead. Mercuric sulfide, probably ground cinnabar, was identified by Bendetti-Pichler (1937) as the red in fossae of incisions in Shang dynasty oracle bones in the Princeton University Collection. Waley (1932) also mentioned the use of cinnabar in early burials in China and described its importance in Chinese alchemy. Johnson (1928) reported it was an important ingredient in recipes for preparing the philosopher's stone. Needham (1970) described its use in elixirs in medieval Chinese pharmacy. There is no doubt that in many ways cinnabar had an important place in arts and early science in China (fig. 2).

Dry-Process Vermilion

The Chinese may have invented this process, and knowledge of it was perhaps carried to the West by the Arabs. Stillman (1960) wrote that, in a Latin manuscript of Greek origin dating from the eighth century sometimes referred to as *Compositiones ad Tingenda* (Lucca, manuscript 490),



Fig. 2 An example of the use of vermilion on a Chinese handscroll, *Tribute Horse and Groom*, by

Chao Yung (1289–c.1360). Dated 1347. Detail. Courtesy Freer Gallery of Art, No. 45.32.

there are many recipes relating to the arts, including one for the preparation of cinnabar by uniting mercury and sulfur. Stillman believed this to seemingly be the first notice of the synthetic preparation of cinnabar in western literature. Kopp (1843–1847) in his *History of Chemistry* added that Geber (or Jabir), the eighth- to ninth-century

Arabic alchemist, spoke of a red compound formed by the union of sulfur and mercury.

In the earliest version of the *Mappae Clavicula* dating from about A.D. 800, there are two descriptions for making artificial cinnabar, the most detailed being in chapter 221C (Hawthorne & Smith, 1974). Thompson (1933) wrote that, "Ar-

addition to the palette of classical antiquity and rules for its manufacture must have been in great demand for some centuries after its discovery." After comparing recipes from various medieval sources he went on to say, "The manufacture of vermilion was a novelty in the eighth century, a commonplace in the fourteenth."

In the Dutch modification of the method, about one hundred parts by weight of mercury are combined in an iron pan with twenty parts of molten sulfur to form black amorphous mercuric sulfide, sometimes called "ethiops mineral," "mohr," or "moor." The black mass, after pulverizing, is slowly charged into earthenware retorts where it is heated to the point where it sublimes (above 580°C) and condenses on earthenware pots or iron cylinders, being converted in the process to the red crystalline modification of mercuric sulfide (α-HgS). The product has only to be treated with a strong alkali solution to remove free sulfur, washed, and then ground under water to prepare it as a pigment. The change from black mercuric sulfide (α' -HgS) to vermilion (α -HgS) is purely physical, involving only a rearrangement of the crystalline structure of the material.

Amsterdam seems to have been the principal center for the manufacture of dry-process vermilion in Europe in the early seventeenth century; a contemporary manuscript describing the methods in detail and including drawings of the furnaces and reaction vessels used was published by Van Schendel (1972). Harley (1982) wrote, "The eighteenth-century customs records show that Dutch vermilion was imported [into England] regularly and in increasing quantities until it reached a peak of just under thirty-two thousand pounds in 1760. After that time it decreased as greater quantities were imported from China and Germany." Blanksma (1948) gave a full review of the various ways of producing vermilion in Holland in the nineteenth and twentieth centuries, with twentyeight references. Mann (1937) also gave a good description of both the dry- and wet-processes, with forty references.

As mentioned, it appears that the Chinese, early in the Christian era, discovered how to combine the elements mercury and sulfur and sublime the initial black product to form the red modification. In the *Tien-kung K'ai-wu*, a treatise on Chinese technology of the seventeenth century by Sung Ying-Hsing (1966), the preparation of mercury from crude cinnabar and the preparation of vermilion from mercury and sulfur by the dry-process



Fig. 3 Edge view of a lump specimen of sublimed dryprocess vermilion purchased in 1970 in Hong Kong, British Crown Colony. The glossy surface of the fragment is shown by light reflected from the brocade on which the specimen lies. The columnar crystal structure is plainly seen on the broken edge, 2.4x.

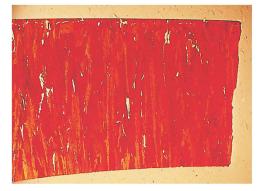


Fig. 4 A thin section of the lump of dry-process vermilion shown in fig. 3, photographed in transmitted light with partially crossed polars, shows voids between the loosely packed columnar crystals, 4.4x.

are described with the aid of woodblock illustrations. According to a brief news item in a British chemical journal, the dry-process, which was described in some detail, was employed in Hong Kong in the late nineteenth century (Journal of the Society of Chemical Industry, 1882). There is good reason to believe it was used in mainland China this century because, on a visit to Hong Kong in 1970, one of the authors (Gettens) was able to buy, in a small color shop, a sample of vermilion, which the proprietor said was made by the dry-process at a town named Shatin in the New Territory. The author became convinced of the dry-process origin of the vermilion when the proprietor gave him a lump of a dark red substance that appeared to be the crude sublimate before grinding. This lump, with smooth parallel sides, showed on the broken edge a closely packed aggregate structure of fine columnar dark red crystals (fig. 3). This might be expected if the sublimate was formed between broken pieces of porcelain, which the news account said were used to pack the crystallization chamber. A thin section made from one of the lumps (fig. 4) shows the columnar crystals clearly and, moreover, shows twinning and fine cracks and cleavages within the crystals. The columnar structure and cleavages of the sublimate are also reflected in the elongated, sliverlike particles in the powder made from it (see fig. 8). Kazuo Yamasaki (private communication) said that production of vermilion began in Japan in 1609 under government monopoly.

Wet-Process Vermilion

According to Kopp (1843–1847), Gottfried Schulz, in 1687 in Germany, discovered that "black ethiops mineral" could be converted to vermilion by heating it in a solution of ammonium or potassium sulfide. This was easier and less costly than the dry sublimation process. Rose (1916) described developments in the process up to the beginning of the century. It apparently became the favorite method of vermilion production in the West, the product being known as both German and English vermilion. It is perhaps the only vermilion-making process in general use in the West today.

Physical Characteristics

The particles of ground cinnabar are quite distinctive in color and general characteristics when viewed microscopically in both reflected and transmitted light. Unless carefully graded by sieving or levigation, the particles are uneven in size and have a distinctly fractured appearance. Cinnabar, which belongs to the hexagonal system, has perfect prismatic {1010} cleavage but uneven fracture. When viewed in strongly convergent light at magnifications upwards of 200x, the transmitted color is bright cherry-red. In the usual mounting media of low and medium refractive index, the edges of the particles are dark (figs. 5A and 6B). Occasionally, in impure specimens, it is possible to see inclusions and seams of colorless matrix mineral, which provides strong evidence that the pigment is natural in origin. The microscopic appearance of vermilion made by the dry (sublimation) method is entirely similar. There is perhaps no certain way to differentiate ground cinnabar and ground dry-process vermilion except possibly on the basis of impurities (figs. 6–8) and perhaps by scanning electron microscopy (see fig. 10).

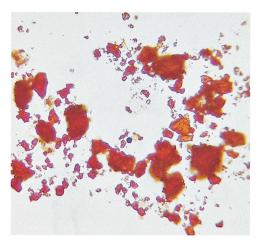
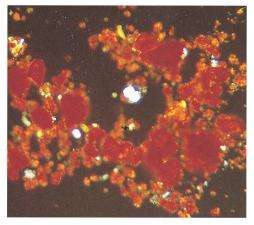


Fig. 5 Ground cinnabar from a painter's pot found at Pompeii (courtesy S. Augusti, Naples) mounted in Canada balsam.

A. By transmitted light using fluorite objective, oil immersion, c. 380x.



B. The same field in crossed polars.

The sample from the drapery of St. John's cloak in Raphael's *Feed My Sheep* was examined using reflected light microscopy at c.450x. (Courtesy of Joyce Plesters, National Gallery, London.)

Wet-process vermilion, on the other hand, is usually fine and uniform in particle size and the particles are individual crystals that have a tendency to form aggregates. They do not have the fractured appearance of ground cinnabar or sublimed vermilion (fig. 9).

The differences in particle character between ground cinnabar and wet-process vermilion are clearly revealed by scanning electron microscopy (fig. 10).

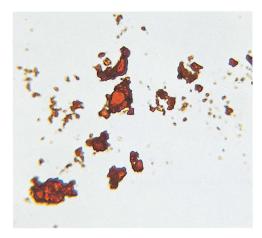


Fig. 6 Particles of vermilion from a red flower in a Japanese screen painting (on paper) in the style of Hanabusa Itcho (1652–1724), Ukiyo-e School. Freer Gallery of Art, No. 03.47. Transmitted light, 531x. Mounted in Canada balsam.

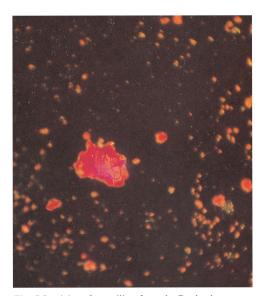


Fig. 7 Particles of vermilion from the Raphael Cartoons for the Sistine Chapel Tapestries in the collection of H.M. Queen Elizabeth II (on loan to the Victoria and Albert Museum, London). The sample is from the drapery of Saint John's cloak in *Feed My Sheep*, by reflected light c. 401x. Courtesy of Joyce Plesters, National Gallery, London.

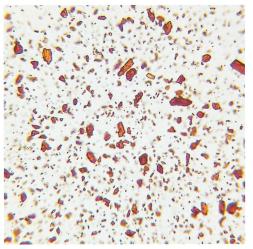


Fig. 8 Dry-process vermilion pigment made by pulverizing a lump of sublimed vermilion similar to that shown in fig. 3. The larger particles tend to be elongated, reflecting the columnar structure of the lump specimen. Oil immersion, transmitted light, 518x. Mounted in Canada balsam.

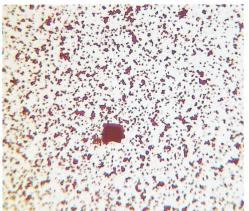


Fig. 9 Modern commercial wet-process vermilion. The tiny particles are fine and uniform in size, which is characteristic of a chemically precipitated product; each particle is an individual crystal. The larger lump in the field is an aggregate of fine particles. Transmitted light, oil immersion, 531x. Mounted in Canada balsam.

Optical Properties

Cinnabar crystallizes naturally in sharply bounded, nearly equidimensional red hexagonal prisms or tablets having strongly positive double refraction and high refractive indices. Dana states that its prismatic {1010} cleavage is perfect. Larsen and Berman (1934) gave the values for refrac-

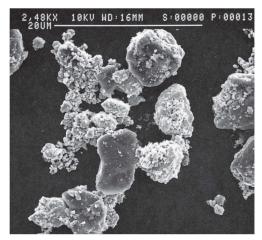


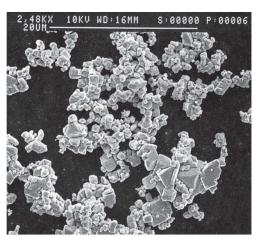
Fig. 10 Scanning electron micrographs of cinnabar and vermilion. Samples from Freer Gallery of Art and Arthur M. Sackler Gallery Dept. of Conservation and Scientific Research pigment collection.

A. Cinnabar, unknown origin, ground in agate mortar,

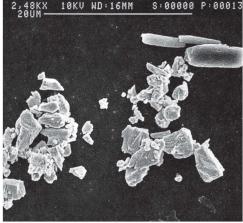
A. Cinnabar, unknown origin, ground in agate mortar, 1950. Sample also contains quartz as determined by x-ray diffraction, printed at 1,686x.



C. Sample as B, showing aggregate of acicular crystals, printed at 440x.



B. Wet-process vermilion, Winsor & Newton, 1970, printed at 1,686x.



D. Dry-process vermilion from a Hong Kong color shop, 1970, printed at 1,686x. Photos: Janet Douglas, Freer Gallery of Art and Arthur M. Sackler Gallery Dept. of Conservation and

tive index as: $\omega L_i = 2.819$; $\varepsilon L_i = 3.146$. The sublimed product has a bluish carmine-red mass color. When it is finely ground, the reflected color approaches orange. By reflected light at high magnification, the red particles have a certain characteristic waxy luster.

Chemical Properties

Scientific Research.

It can be observed that in small quantities under the microscope, red mercuric sulfide is unaffected by dilute and concentrated nitric, hydrochloric and sulfuric acids even when warmed to dryness, but it is readily decomposed on moderate warming with aqua regia to form white opaque crystalline

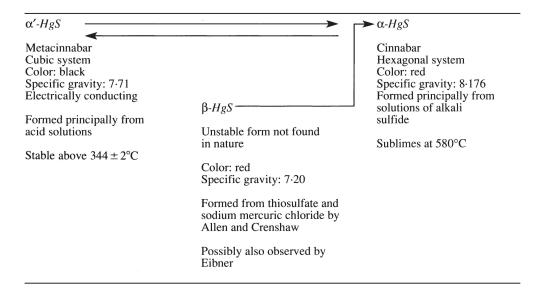
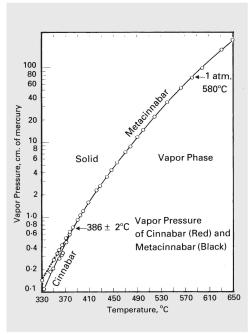


Fig. 11A. Summary of the properties and relationship of the various crystalline forms of mercuric sulfide.



B. Phase diagram of cinnabar (red) and metacinnabar (black) according to data of J. Rinse. *Rec. Trav. Chim.* 47 (1928), 28.

mercuric chloride (see fig. 18). The pigment is, likewise, unaffected by alkalis.

Permanence and Compatibility with Other Pigments and with Paint Media

Despite of the fact that vermilion is a sulfide, it is remarkably unreactive with other pigments (Gettens & Sterner, 1941). In oil-medium, it was commonly used with lead white to produce flesh tints with no sign of formation of black lead sulfide. It was used on alkaline lime fresco walls.

Vermilion was considered to be a lightfast pigment by the German Society for Promotion of Rational Painting Techniques (Munkert, 1905) and the United States Commercial Standard CS 98–62 (U.S. Department of Commerce, 1962), yet authorities today do not generally consider it to be a "permanent" pigment, for it has been known since Roman times that specimens may darken in an apparently capricious manner. Numerous examples in paintings, nevertheless, testify to its essential stability, and samples have been observed to withstand exposure to sunlight for at least ten years (Eibner, 1926).

Rasti and Scott (1980) have shown that vermilion appears to accelerate the photo-oxidation of linseed oil films.



Fig. 12 The darkening of vermilion on easel paintings. A. Detail from Nardo di Cione's *Altarpiece: Three Saints*, painted in egg tempera on panel, c. 1365. The lining of the saint's drapery is in vermilion, now discolored. National Gallery, London, No. 581. Reproduced by permission of the Trustees.

B. Detail from Cuyp's *A Hilly River Landscape*, painted in oil on canvas, late 1650s. National Gallery, London, No. 53. Reproduced by permission of the Trustees.

Darkening of Vermilion

Under normal conditions, mercuric sulfide exists in two principal crystalline modifications, the red cinnabar (α -HgS) and the black metacinnabar (α '-HgS). An unstable red form (β -HgS) has also been reportedly synthesized in the laboratory (Allen & Crenshaw, 1912). The interrelationship between these crystalline forms is summarized in figure 11. At pressures above 130kbar, cinnabar transforms to a new phase with the sodium chloride structure (Huang & Ruoff, 1983).

Although it is the red form that is wanted by artists, most methods of synthesizing the compound first yield the black form, which must be sublimed or digested to produce the red variety. Detailed studies by Eibner in 1912–1918 showed that digestion in alkali polysulfides facilitated the transition of the black to the red, but that impurities in the digestion liquor, particularly thiosulfate, led to considerable instability of the red form (Eibner, 1917–1918). It was shown by Daniels (1987) that alkali metal halide impurities in vermilion are particularly effective in catalyzing the

transformation. Both rubbing (trituration) and exposure to light promote the conversion to metacinnabar.

Exposure to light of wavelength 400 to about 570 nm, the region in which cinnabar absorbs light, will induce darkening which, to a certain extent, is reversible in the dark. In controlled experiments, darkening has been found to be more rapid in paints that allow the light to penetrate below the surface. Joyce Plesters (private communication), however, states that of the samples she encountered, the darkening of vermilion occurs mainly in paintings in egg tempera. A clear instance may be seen in a drapery of Nardo di Cione's Altarpiece: Three Saints (fig. 12A) in the National Gallery, London (no. 581) (Gordon et al., 1985). However, the phenomenon is not unknown in oil paintings, for example in Aelbert Cuyp's A Hilly River Landscape (fig. 12B) also in London (no. 53), in which the vermilion of the huntsman's red coat is seen to be patchily discolored by the formation of metacinnabar, although the darkening was determined to have been caused by only a very thin coating around the surfacemost

particles of unchanged pigment (Plesters et al., 1982). Because the change is so superficial in this case, detection of the metacinnabar by x-ray diffraction was not possible (Plesters et al., 1982). Plesters also reports that one of the most striking cases appeared in the red-painted borders of the interior decoration in a late Byzantine church in Cyprus, where the light coming from small clerestory windows was low. There was obvious darkening in the powdery distemper paint wherever the surface was turned toward the light, but it remained bright red in the undercutting of the molding. She also mentioned that just perceptible darkening is found in one or two areas of vermilion in the Raphael Cartoons in the Queen's Collection (on loan to the Victoria and Albert Museum), painted in animal glue medium.

The traditional use of red glazes of madder, kermes, and cochineal lakes over vermilion underpaint not only increases the purity (chroma) of the color but has been shown to reduce the tendency to darken. An extensive review of the darkening phenonmenon has been prepared by Feller (1967).

Color and Spectral Reflectance

Because of its high refractive index, vermilion is a pigment with high light-scattering power and, hence, excellent hiding ability. The brightest pigments vary in masstone color from strong red to vivid reddish orange, in the range of Munsell 5R to 7.5R, possessing CIE chromaticity coordinates from about $x\!=\!0.55$, $y\!=\!0.34$ to $x\!=\!0.54$, $y\!=\!0.32$ (Illuminant C) (Feller, 1967). The dominant wavelength for the bright pigment varies between 605 and 615 nm; the purity is about 67%. Vermilion is such a high-chroma pigment that Thompson (1956) stated that correspondingly vivid pigments such as azurite and malachite were necessary to balance it in the medieval artist's palette.

The spectral reflectance curves in the visible region of bright, medium, and dark varieties are shown in figure 13. The reflectance curves of the darkened states of bright vermilion are similar to those of the dark and medium varieties, making it difficult, if not impossible, to distinguish in this way whether the dark color of a vermilion paint is in its original or a darkened state, unless upon examination of its cross section it is observed that the darkened form is primarily on the surface rather than throughout the paint.

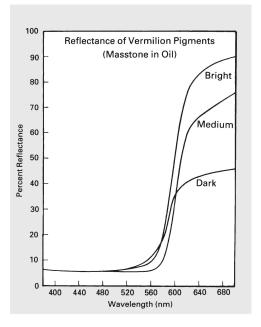


Fig. 13 Spectral reflectance curves of bright, medium, and dark varieties of vermilion.

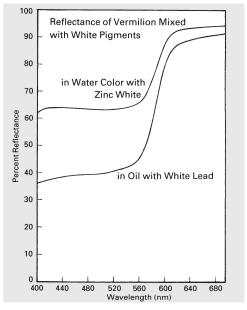


Fig. 14 Typical reflectance curves of vermilion mixed with white pigments.

Typical curves of vermilion mixed with white are shown in figure 14, a combination that yields hues of pink, widely used for flesh color (Feller, 1967). Because of its high hiding power and chroma, the pigment stands out strongly in paint-



Fig. 15 Detail of Saint Jerome's vermilion drapery from part of an altarpiece attributed to Masolino. National Gallery, London, No. 5962. Reproduced by permission of the Trustees.

ings and lends brilliance and contrast (figs. 2, 15, 16, and 17).

Vermilion is a band-gap semiconductor with an energy of the gap in the medium range of 2.0 eV. Consequently, all wavelengths of light but the red are absorbed by the material. Where the band-gap energy is even smaller, below 1.77 eV (equivalent to a wavelength of 700 nm), all visible light is absorbed and the compound is black in color, as in the case of metacinnabar, which has a band-gap energy of 1.6 eV (Nassau, 1983). The cadmium sulfide and sulfoselenide yellow, red, and orange pigments owe their color to the same cause (Nassau, 1983).



Fig. 16 Titian's *Bacchus and Ariadne*. Detail showing the vermilion red scarf of Ariadne. National Gallery, London, No. 35. Reproduced by permission of the Trustees.

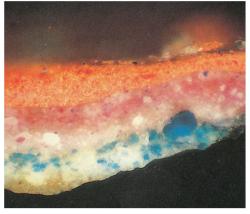


Fig. 17 Cross section of a sample of vermilion paint from the scarf of Ariadne in *Bacchus and Ariadne* by Titian, a detail of which is shown in fig. 16. In reflected light, c. 893x. The uppermost layer is coarsely ground vermilion of the red scarf in linseed oil medium.



Fig. 18 Mercuric chloride from the partial decomposition with aqua regia of a specimen of vermilion from a Japanese painting (Freer Gallery of Art, No. 70.30). This is an intermediate step in the test for mercury by the cobalt mercuric thiocyanate reaction. Specimen not mounted. Photographed by reflected light without cover glass, 27x.

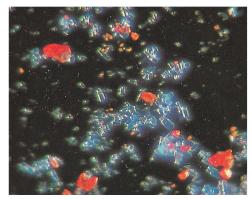


Fig. 19 Crystals of cobalt mercuric thiocyanate, Co(SCN)₂.Hg(SCN)₂ obtained in testing for mercury in a sample of cinnabar from Pompeii. Mounted in Canada balsam. Photographed in reflected light, 340x.

Microchemical Analysis

Various methods have been used to identify both the mercury and the sulfur constituents of vermilion. In most of them, the red sample must first be converted to a soluble mercuric salt.

Decomposition with Aqua Regia

If preliminary tests show that the red is insoluble in both warm concentrated hydrochloric acid and nitric acid used separately, it can easily be broken down by adding a tiny drop each of both concentrated hydrochloric and nitric acids (or preferably in the ratio 3:1) to a few particles on a microscope slide and then warming. Fine particles of vermilion will decompose rapidly with one treatment but coarser particles require two or more. The residue of mercuric chloride (HgCl₂) formed by the reaction is white and crystalline. If evaporation is slow enough, a ring of dendritic crystals forms at the edge of the drop (fig. 18).

Vermilion can easily be differentiated from haematite by the ready solubility of the former in a drop of dilute nitric acid to which a crystal of potassium iodide has been added. The reagent rapidly dissolves vermilion but has no effect on ferric oxide (Elisabeth FitzHugh, private communication). This solubility of HgS in hydriodic acid apparently was first observed by Kekulé (1862).

Double Thiocynate Test for Hg²⁺

In practice, this is perhaps the most satisfactory and convenient test, but it requires experience. A drop of distilled water about 2 mm in diameter is placed on the slide about 1 mm distant from the white crystalline residue obtained from the aqua regia treatment. To this test drop are added a few crystals of powdered cobalt acetate (or other soluble cobalt salt) and then one or two crystals of potassium thiocyanate (KCNS). Since the test drop must be quite concentrated with Hg²⁺ ions, it is drawn with the end of a fine glass droppingrod across the white residue. The presence of mercury is shown by the formation in a few seconds (usually not immediately) of deep blue prisms, spherulites, and dendrites of cobalt mercuric thiocyanate, Co(SCN), Hg(SCN), (fig. 19). The formation of a pale bluish crystalline residue on drying must not be taken as a test. Only the bright blue crystals that remain when the residue is taken up with water or 1% HNO3 are to be regarded as containing mercury. Short (1948), who used a slightly different technique, claimed that the limit of detection is 0.005% HgCl₂ in 1% HNO₃. Short showed in his plate 14 good color photomicrographs of the test at 210x magnification.

Other Tests for Hg²⁺

Plesters (1955–1956) employed a spot test. The white residue after breakdown with hot concentrated HCl is redissolved in a drop of dilute HNO $_3$. One drop of this solution is placed on a filter paper impregnated with a freshly prepared diphenylcarbazone reagent (1% in ethanol). A violet–blue coloration indicates Hg²⁺.

On the other hand, Benedetti-Pichler (1937) identified mercury in tiny samples of cinnabar

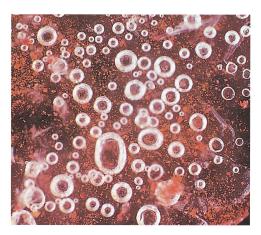


Fig. 20 The release of bubbles of nitrogen from sodium azide—iodine reagent used to test for the presence of sulfur (sulfide) in vermilion from a fragment of Roman wall painting from the Palatine. Sample courtesy of H. J. Plenderleith. Photographed without cover glass in reflected light, 121x.

from Chinese oracle bones by using Emich's test, in which the mercury in the residue after oxidation and solution by bromine vapors is reduced by a copper wire and amalgamated to it; then the mercury is distilled by heating the wire in a glass capillary tube, and it is recognized microscopically in the form of fine droplets of liquid mercury on the inner surface of the tube. The reader is advised to consult the original article for further details.

Sodium Azide-Iodine Test for Sulfide

Ordinarily, it is not necessary to test for sulfur if it is reasonably certain from microscopic examination that vermilion is present, and if Hg^{2+} can be established with certainty. Plesters (1955–1956) confirmed S^{2-} by using a drop of sodium azide—iodine reagent (1g NaN3, 1g KI, and a small crystal of I_2 in 3 ml water). If sulfide is present, it catalyzes the reaction $2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$ with release of bubbles of nitrogen that cluster at the surface of the red particles (fig. 20); simultaneously the orange color of the reagent fades because of consumption of free iodine. Feigl (1946) described this test in some detail: "The fact that soluble as well as insoluble sulfides exert this catalytic action is of considerable analytical value."

Sulfate Test for Sulfur

This was used by Benedetti-Pichler (1937) in testing for sulfide in the powdered cinnabar used as pigment in the oracle bones of China in the Princeton University Collection. A drop of 1% calcium

chloride solution is added to a tiny specimen of the red confined to a 2 mm diameter area on the microscope slide. The slide is inverted and placed over the opening of a bottle of bromine water. After 5 minutes the droplet turns brownish due to excess of bromine dissolved. When the droplet is examined under a microscope, all the red particles may have disappeared, leaving colorless particles of quartz and other impurities. After a short time, bundles of needlelike crystals of gypsum $(CaSO_4.2H_2O)$ appear, which show the presence of SO_4^{2-} produced by the oxidation of sulfide.

Substitution and Sophistication

Perhaps because of its cost and also because of the poor lightfastness of some varieties, vermilion has long been substituted and sophisticated by addition of red lead, chrome orange, and organic colorants. According to Mundt (Munkert, 1905) "carmine vermilion" was often a mixture of red iron oxide and vermilion. Under the name "American vermilion," chrome orange pigments and mixtures of red lead and lakes have been sold. Antimony vermilion (Sb₂S₃), presumably as a substitute for true vermilion, was introduced in England in 1847 (Boxall, 1978) but probably never attracted widespread use. The lakes alone, based on monolite red, lithol reds, eosin, and other synthetic dyes of appropriate hue were once, according to Hurst (1906), called "vermilionettes." Gettens (1954) reported finding two such reds, one based on toluidine red, the other on a mixture of eosin and 1-(o-chloro-p-nitrophenylazo)-2-naphthol struck on barytes, on purportedly early Chinese ceramic objects (see also Freeman & Graichen, 1954).

From the 1950s, a range of dark red to bright orange colors, based on mixed crystalline compounds of mercuric sulfide and cadmium sulfide (CdS.xHgS), have been introduced by Hercules, Inc., in the United States, and termed by the manufacturer as "Mercadmium" pigments (Moore, 1973).

Criteria for Certain Identification

No identification of artists' pigments may be considered complete without microscopic examination, for this reveals the state of purity, particle size, morphological characteristics, and the presence of other pigments, either in major or minor amounts. In the majority of instances, vermilion or cinnabar can be recognized microscopically by its color and optical properties, provided it is ob-

Table 1 X-ray Diffraction^a Data for Cinnabar and Metacinnabar

Cir	Cinnabar (hexagonal) ^b			Metacinnabar (cubic) ^c		ır (cubic) ^c	
d (Å)	I	d (Å)	I	d (Å)	I	d (Å)	I
3.59	6	1.1614	4	3.38	100	1.0344	2
3.35	100	1.1358	2	2.926	35	0.9891	6
3.16	30	1.1271	4	2.068	55	0.9753	2
2.863	95	1.1201	4	1.764	45	0.9252	4
2.375	10	1.1047	6	1.689	10	0.8923	2
2.074	25	1.0828	2	1.463	8	0.8824	2
2.026	12	1.0693	2	1.342	12	0.8447	4
1.980	35	1.0309	4	1.3085	10	0.8194	4
1.900	4	1.0132	2	1.1945	10		
1.765	20	0.9910	<1	1.1263	8		
1.735	25	0.9859	4				
1.679	25	0.9753	4				
1.583	6	0.9599	4				
1.562	6	0.9503	4				
1.433	8	0.9400	4				
1.401	2	0.9184	3				
1.358	6	0.9103	1				
1.344	12	0.8981	1				
1.305	10	0.8821	1				
1.269	4	0.8642	1				
1.258	8						
1.248	4						
1.1975	2						
1.1883	4						
1.1787	4						

(Courtesy of JCPDS International Centre for Diffraction Data)

served in a properly prepared mount that permits examination of individual particles by strong transmitted and reflected light.

Mercuric sulfide may be positively identified by x-ray diffraction analysis (see table 1). The detection of mercury by emission spectrographic analysis or any of the microchemical tests described makes the identification highly probable, but such tests should be accompanied by a sodium azideiodine test for sulfide sulfur. The pigment may be distinguished from modern "Mercadmium" red, or from mercuric iodide by observing their optical properties under the microscope, and by the presence of cadmium in the former and the ready solubility of the latter in dilute nitric acid.

As already stated, no positive way is known at present by which natural and dry-process synthetic pigment may be distinguished, although "inert" mineral impurities usually indicate the mineral variety. The particles of cinnabar and dryprocess vermilion are generally irregular fragments, whereas synthetic wet-process vermilion particles are usually small and equant, although the distinction is not always clear by optical microscopy.

Emission Spectrometric Analysis

The prominent lines for mercury in the direct current arc are: 5460.74, 4358.35, 4046.56, 3663.27, 3654.83, 3650.15, and 2536.52 Å (M.I.T. Wavelength Tables, 1963). The line at 2536.52 Å is particularly strong. The limit of identification is 0.1% (Waring & Annell, 1953).

a. Cu, Kα radiation at 26°C

b ICPDS File No. 6-256

c. JCPDS File No. 6-21

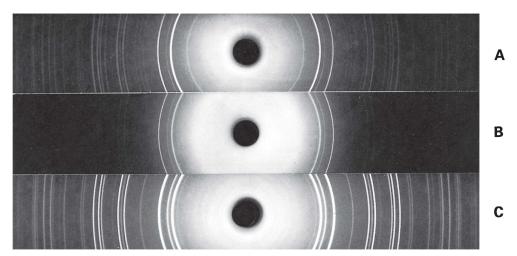


Fig. 21 X-ray diffraction patterns for vermilion.

A. Cinnabar mineral. New Idria Mine, San Benito
County, California. Department of Mineral Sciences,
Smithsonian Institution collection. Quartz lines marked.
B. Vermilion. Red pigment. Japanese Buddhist Sutra,

early Edo period, 1666. Freer Gallery of Art, No. 62.27. C. Vermilion. Commercial powder pigment made by the wet process. Winsor & Newton, 1970. Photographs not be used for measurement purposes. Powder patterns by Elisabeth West FitzHugh.

X-ray Diffraction Analysis

Vermilion, as a crystalline compound, is easily identified by x-ray diffraction analysis. The spacings and intensities of synthetic vermilion measured by Swanson, Fuyat, and Ugrinic, which are listed in the *JCPDS Powder Diffraction File*, are shown in table 1 with the data for black metacinnabar. X-ray diffraction studies of natural cinnabar (Aurivillius, 1950) and synthetic mercuric sulfide (Swanson et al., 1955) have not revealed any structural differences. Some examples are shown in figure 21.

X-ray Spectrometric (X-ray Fluorescence) and Electron-Probe Microanalysis

The main lines for mercury are: $L\alpha_1$, $L\alpha_2$:10 keV, 9.9 keV; $L\beta_1$, $L\beta_2$: 11.8 keV, 11.9 keV; $L\gamma_1$: 13.8 keV (*Handbook of Spectroscopy*, 1974).

Infrared Spectrophotometry

Because of its high refractive index, vermilion does not readily lend itself to the usual methods of obtaining an infrared spectrum. Van Asperen de Boer (1969 and 1970), however, has published curves of the reflectance and hiding thickness of vermilion in linseed oil at wavelengths from 700 to 2,500 nm.

Spectral plots in the far infrared have been obtained by Karr and Kovach (1969) for cinnabar

and synthetic mercuric sulfide using a micropelleting technique. In the spectra of both forms, strong bands are observed at 340 and 123 cm⁻¹, with medium-intensity absorptions at about 277 and 87 cm⁻¹. A weak feature at 38 cm⁻¹ is also recorded.

X-radiography

Because vermilion is a dense pigment, areas painted with it often show strong contrast (absorption) on radiographs. The mass absorption coefficient, μ/ϱ , of vermilion pigment at wavelength 0.709 Å is 114.5 and 95.53 for vermilion oil paint (Rees Jones, 1960), rather higher than for lead white (see chapter 3).

Trace Elements by Neutron Activation Analysis

J.P.W. Houtman of the Technical University at Delft (private communication) has kindly provided preliminary data on trace elements to be found in vermilion. Zinc and arsenic were found at concentrations of about 10 ppm; antimony, copper, and manganese were found at about 1 to 3 ppm in seven samples of nineteenth- and twentieth-century pigments examined. Silver, nickel, and chromium were absent in nearly all samples.

Paint layers containing vermilion were reported to produce sharp but low-intensity images in neutron autoradiographs through the formation of ²⁰³Hg (half-life, 48 days) (Meyers et al., 1982).

Notable Occurrences

Vermilion in Western Paintings

Date	Artist/School, Title, Description, Collection or Location	Analyst and Method of Identification
1st C A.D.	Roman, wall painting fragment from the Palatine, Freer Gallery of Art Technical Laboratory	R. J. Gettens micr.
1st C A.D.	Various Roman and Pompeiian wall paintings	E. Raehlmann (1914) micr.
1st C a.d.	Dry color in pigment jar found at Pompeii, National Museum, Naples	S. Augusti (1967) micr.
1st/3rd C A.D.	Egyptian, Fayum painting <i>Portrait of a Woman</i> , Princeton University	R. D. Buck (private communication) micr.
14th C	Byzantine wall painting Church of Kariye Çamii, Istanbul	R. J. Gettens (Gettens & Stout, 1958) micr.
14th–15th C Italian	Spinello Aretino, attrib. Madonna and Child Enthroned with Angels Fogg Art Museum, 1905.1	R. J. Gettens (1947) micr.
14th–19th C	439 European paintings, numerous artists, various schools, Bavarian State collection	H. Kühn (private communication)
1450-1800	23 paintings by Dutch Masters Dutch Museums and private collections	A. M. de Wild (1929) micr.
15th C	Jan van Eyck Polytych of the Mystic Lamb Church of St. Bavon, Ghent	P. Coremans (1953) micr.
15th–16th C	Bellini, Tintoretto, Titian	E. Raehlmann (1914) micr.
15th–16th C Italian	Girolamo de Benvenuto Madonna and Saints Fogg Art Museum, 1927.206	R. J. Gettens micr.
17th C	Peter Paul Rubens Descent from the Cross Antwerp Cathedral	P. Coremans and J. Thissen (1962) micr.
17th C	Jan Vermeer Several paintings, private and public collections	H. Kühn (1968)

micr. = Identification with the microscope

Vermilion^{a,b} in Easel Paintings in the Collection of the National Gallery, London*

Date	Artist and Title	Acquisition Number
late 13th C	Ascribed to the Master of San Francesco Crucifix	6361
c.1300	Duccio Triptych: The Virgin and Child with Saints	566
c.1300	Duccio The Virgin and Child with Four Angels	6386
c.1300	Ascribed to Giotto Pentecost	5360
1308–1311	Duccio The Transfiguration (predella panel from the Maestà)	1330
c.1325	Ugolino di Nerio Two Angels (spandrel from an altarpiece)	6486
c.1365	Nardo di Cione Altarpiece: Three Saints ^c (see fig. 12A)	581
after 1365(?)	Master of the Lehman Crucifixion Noli me Tangere	3894
1374 (s.& d.)	Barnaba da Modena The Coronation of the Virgin, The Trinity, The Virgin and Child, The Crucifixion	2927
1425/1435(?)	Ascribed to Masolino Sts. John the Baptist and Jerome (part of an altarpiece) (see fig. 15)	5962
1437–1444	Stefano di Giovanni, known as Sassetta The Pope Accords Recognition to the Franciscan Order (panel from an altarpiece)	4759
2nd quarter 15th C	Piero della Francesca The Baptism of Christ	665
2nd quarter 15th C	Rogier van der Weyden The Magdalen Reading (fragment of an altarpiece)	654

^{*}Table compiled by J. Plesters and A. Roy, National Gallery, London. Identification was made by means of examination of optical properties and particle characteristics combined with microchemical tests and in some cases spectrographic analysis or x-ray diffraction

Attributions and dates are based on the catalogues of the National Gallery, London. "(s.&d.)" signifies that the work is signed and dated by the artist.

a. Many of the occurrences listed above were from areas of red drapery or costume in the pictures, but other uses were noted; for instance, the rosy cheeks of the Christ Child in the Titian Madonna and Child (no. 3948) owe their color to vermilion.

b. Most of the samples of vermilion identified in the list of occurrences given above had the particle characteristics associated with either the ground cinnabar mineral or the synthetic form prepared by the dry process, these two forms being microscopically difficult to distinguish. Samples from two nineteenth-century pictures examined by SEM, Monet (no. 6456) and Van Gogh (no. 3861), suggest the use of wet-precipitated vermilion.

c. In these pictures some areas of vermilion (though not all) appear to have darkened slightly on the surface. Although under the microscope at c.150x the discoloration appears as a very thin, irregularly distributed layer of blackish particles, the visual effect on the picture is rather that of a purplish gray bloom with a slightly metallic sheen, rather than true blackening (see Plesters et al., 1982). In the picture ascribed to Michelangelo (no. 809) the vermilion, which occurs on an angel's sash, is of a strikingly orange hue and quite finely ground, whereas in the Uccello "Battlepiece" (no. 583) the vermilion is of a deep, almost crimson tone and comparatively coarsely ground. A common factor is that the areas of paint in which darkening has occurred are in egg tempera medium. Darkening of vermilion in oil paintings is rare, examples being more frequent in paintings in aqueous media or in wall paintings. The Aelbert Cuyp (no. 53), is an unusual case of an oil painting that shows the phenomenon.

Date	Artist and Title	Acquisition Number
1450s	Paolo Uccello Niccolò Mauruzi da Tolentino at the Battle San Romano (from a series) ^c	583
1454–1469	Piero della Francesca St. Michael (panel from a polyptych)	769
c.1455	Dieric Bouts The Entombment	664
1460s	Giovanni Bellini The Blood of the Redeemer	1233
1463/1482(?)	Giovanni di Paolo Sts. Fabian and Sebastian	3402
mid/late 1460s	Giovanni Bellini The Agony in the Garden	726
1470/1480(?)	Hans Memling St. Lawrence (wing of an altarpiece)	747
c.1473	Francesco del Cossa St. Vincent Ferrer	597
3rd quarter 15th C	Sandro Botticelli The Adoration of the Kings	592
c.1475	Ascribed to Antonio and Piero del Pollaiuolo Altarpiece: The Martyrdom of St. Sebastian	292
c.1480	Cosimo Tura The Virgin and Child Enthroned (central panel of an altarpiece)	772
c.1480s	Sandro Botticelli Portrait of a Young Man	626
c.1491	Luca Signorelli Altarpiece: The Circumcision	1128
last decade 15th C	Ascribed to Michelangelo Madonna and Child with St. John and Angels ^c	809
1500 (s.& d.)	Sandro Botticelli The Mystic Nativity	1034
c.1500	Master of St. Giles The Mass of St. Giles	4681
1500/1515	Jan Gossaert The Adoration of the Kings	2790
1503	Raphael The Crucifixion	3943
1504	Cima da Conegliano The Incredulity of St. Thomas	816
1506/1515(?)	Michelangelo The Entombment	790
1512 (s.& d.)	Hans Baldung Grien The Trinity: A Mystic Pietà	1427
1517–1519	Sebastiano del Piombo The Resurrection of Lazarus	1

Date	Artist and Title	Acquisition Number
c.1520s	Lorenzo Lotto Virgin and Child, with Sts. Jerome and Anthony of Padua	2281
1522–1523	Titian Bacchus and Ariadne (see fig. 16)	35
1st quarter 16th C	Titian The Holy Family	4
early 16th C	Perugino Altarpiece: The Virgin and Child	288
c.1530s(?)	Lorenzo Lotto The Prothonotary Apostolic, Giovanni Guiliano	1105
1543–1544	Tintoretto Jupiter and Semele	1476
1547	Lorenzo Lotto Family Group	1047
2nd quarter 16th C	Lucas Cranach the Elder Cupid Complaining to Venus	6344
mid-16th C	Ascribed to Niccolò dell'Abbate The Story of Aristaeus ^d	5283
16th C	Bronzino Madonna and Child with the Baptist and St. Anne or St. Elizabeth	5280
1561–1562	Paolo Veronese The Consecration of St. Nicholas	26
1570s	Titian Madonna and Child	3948
c.1578	Tintoretto The Origin of the Milky Way	1313
c.1580/1585	Tintoretto Portrait of Vincenzo Morosini	4004
c.1609	Peter Paul Rubens Samson and Delilah	6461
c.1615	Guido Reni Lot and His Daughters Leaving Sodom	193
1620s	Peter Paul Rubens Triumph of Julius Caesar	278
1627 (s.&d.)	Hendrik ter Brugghen Jacob and Laban	4164
1629/1630	Peter Paul Rubens Minerva Protects Pax from Mars	46
1630s	Francisco de Zurbarán St. Margaret	1930

d. This is a rare occurrence of vermilion in the ground or preparation on the canvas of the picture. The ground in this case consisted of a rather thin layer of lead white oil paint containing scattered particles of charcoal black and vermilion. To the unaided eye this mixture has a mauvish gray tone. There are, incidentally, no conspicuous areas of vermilion in the upper paint layers that constitute the pictorial design.

Date	Artist and Title	Acquisition Number
c.1630/1640	Peter Paul Rubens The Judgment of Paris	194
c.1635/1640	Peter Paul Rubens The Rape of the Sabine Women	38
1636–1638	Rembrandt Belshazzar's Feast	6350
c.1640	Philippe de Champaigne Triple Portrait of Cardinal Richelieu	798
c.1652	Follower of Rembrandt An Old Man in an Armchair	6274
c.1655/1660	Aelbert Cuyp A Hilly River Landscape with a Horseman Talking to a Shepherdess ^c (see fig. 12B)	53
c.1735	Canaletto Venice: The Feastday of St. Roch	937
1743	William Hogarth Marriage à la Mode	114–116
mid-18th C	Giovanni Battista Tiepolo An Allegory with Venus and Time	6387
1770–1772	Joseph Wright of Derby Mr. and Mrs. Coltman	6496
c.1811	Jean Auguste Dominique Ingres M. de Norvins	3291
1869 (s.&d.)	Claude Monet Bathers at La Grenouillère	6456
1877	Claude Monet The Gare St. Lazare	6479
1878 (s.&d.)	Edouard Manet The Waitress	3858
c.1879	Pierre Auguste Renoir The Seine at Asnières	6478
c.1886	Paul Cézanne Mountains in Provence	4136
1889	Vincent van Gogh A Cornfield with Cypresses	3861
after 1916	Claude Monet Water-Lilies	6343

Vermilion and Cinnabar in Near Eastern and Indian Paintings

		8
Date	Artist/School, Title, Description, Collection or Location	Analyst and Method of Identification
a.d. 977	Persian MS. page from <i>Book of Enoch</i> , Isfahan Cleveland Museum of Art	R. D. Buck (private communication) micr.
15th–18th C	Various Persian and Indian illuminated manuscripts and miniature paintings Freer Gallery of Art	R. J. Gettens micr.
17th C	Moghul Indian wall painting Akbar's Tomb at Sikandra near Agra	J. C. Nagpall (1964)
Vermilion and C	innabar in Far Eastern Objects and Ind	ian Paintings
2nd millennium B.C.	Early Chinese Oracle bone inscriptions, Princeton University	A. A. Benedetti-Pichler (1937) micr.
2nd millennium B.C.	Early Chinese Oracle bone inscriptions, Royal Ontario Museum, Toronto	B. Leech (private communication) x-ray diffraction
1st millennium B.C.	Chang-sha site in China Lacquer objects, Freer Gallery of Art Technical Laboratory	R. J. Gettens micr.
7th C A.D.	Japan Hōryūji temple near Nara Wall paintings, Buddhist figures (sampling done before partial destruction of the paintings by fire in 1949)	K. Yamasaki (1948) micr.
9th–10th C A.D.	Wall paintings, Buddhist subjects Western China at Dun-huang. Paintings from the cave: "Halls of the Thousand Buddhas," British Museum, London, Aurel Stein Collection	R. J. Gettens micr.
10th C A.D.	Chinese temple painting Wall painting, Nelson-Atkins Museum of Art, Kansas City	R. J. Gettens (Sickman, 1952) micr.
13th–19th C	Numerous Chinese and Japanese paintings on paper and silk, Freer Gallery of Art, Washington	R. J. Gettens micr.
Vermilion and C	innabar in American Paintings	
early 19th C	Spanish wall paintings Floral and geometric designs	R. J. Gettens (Steen & Gettens, 1962) micr.

micr. = Identification with the microscope

Tumacacori Mission church, Arizona

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Malachite and Green Verditer

RUTHERFORD J. GETTENS and ELISABETH WEST FITZHUGH

Current Terminology

English: malachite German: Malachit Spanish: malaquita French: malachite (f.) Italian: malachito Russian: Manaxut Japanese: rokusho Chinese: shih lü (March, 1935)

The name malachite is derived from the Greek $\mu\alpha\lambda\alpha\chi\dot{\eta}$, mallows, in allusion to its color (Palache et al., 1951).

Obsolete Terms and Synonyms

Names given are: chrysocolla, molochites (Agricola) (Hoover & Hoover, 1950); mountain green, Berggrün, verde azzurro (Thompson 1962); verdetto della Magna, Hungarian green, mineral green; also Bremen green, copper green, iris green, Olympian green, verditer green, and green bice. The name malachite green is also given to a triphenylmethane dye (CI Basic Green 4) and related compounds; some are water soluble and are used as biological stains (Colour Index 1956 and 1957; Pratt, 1947).

Composition and Structure

The mineral, basic carbonate of copper, CuCO₃.Cu(OH)₂ occurs in such large masses that it is usually quite pure.

Elucidation of the structure of malachite by x-ray crystallography has shown the coordination around the copper atoms to be square-planar with two further oxygens at a slightly greater distance to give an elongated tetragonal dipyramid. The co-

ordination polyhedron may be explained by Jahn-Teller distortion of an octahedron due to the 3d⁹ electronic configuration of Cu²⁺ (*Handbook of Geochemistry*, n.d.). It might be noted that malachite is not a copper complex but structurally is an infinite three-dimensional array of Cu²⁺, OH⁻, and CO₃⁻ ions (Wells, 1984).

Sources

Malachite is a mineral found in many parts of the world in the upper oxidized zones of copper ore deposits. It is usually associated in nature with azurite (see chapter 1), the blue basic carbonate of copper 2CuCO₃.Cu(OH)₂, which contains less chemically bound water, and also with chrysocolla (copper silicate). Malachite is more abundant in nature than is azurite. Large deposits have been found in the Ural Mountain region of the former U.S.S.R., in the Katanga district of Zaire (formerly the Belgian Congo, see fig. 1), in Zimbabwe, formerly Rhodesia, and also in Chile.



Fig. 1 Hand specimen of malachite from Zaire (formerly Belgian Congo). Author's collection (RJG). Photo: Raymond A. Schwartz.

These have been important sources of malachite for lapidary purposes in recent times. The sources of malachite used in medieval European painting are not well known, although there is sparse mention of copper mines in Hungary being a probable source of both azurite and malachite, and it is well known that there were ancient copper mines in East Central Europe. Chessy, near Lyon in France, may have been another source. Vanoccio Biringuccio, the fifteenth-century Italian metallurgist, spoke of "green azure," which the translator said is probably malachite; it is related to "German azure," (azurite). In the Smith and Gnudi translation (1943, p. 118) it says:

This is more or less green or blue according to the quantity of mixture and more or less abundant according to the powerful exhalation of the ore. It is also gathered with care from the colored stones and is cleaned and made fine by washing and grinding. That which is the finest and of the loveliest color is the most highly esteemed by the master painters.

There are many small deposits of copper ores both in China and Japan that may have served as sources of malachite. We are told, however, that modern color dealers in Japan get their malachite from Africa and Chile.

History of Use

Lucas (1962) wrote that malachite was used in Egypt for eye-paint as early as predynastic times and has been found on tomb paintings since the Fourth Dynasty; it occurs on Sinai and in the Eastern Desert. It is somewhat curious that malachite, in spite of greater natural abundance, does not appear to have been used in European painting nearly so extensively as azurite. Harley (1982) pointed out, moreover, that malachite is also less frequently mentioned than azurite in written sources. The reason, she thought, is that to be useful as a bright green it must be ground coarse, because, if finely ground, it becomes too pale for practical use. Perhaps this is true. Being moderately low in refractive index, it was more satisfactory in tempera than in oil-medium. The early examples of artificial malachite, which have been found on easel paintings, have been generally in egg tempera medium (Notable Occurrences). Thompson (1936, p. 161) also described its sparse mention in medieval literature. It may also be true that artificial copper greens, like verdigris and copper resinate made from malachite or other copper minerals, were more satisfactory greens, especially in oil- or in oil-resin media (Kühn,

1964). Joyce Plesters (private communication) suggested that, like verdigris, copper carbonate, when finely divided, may sometimes react with oil- or oil-resin media to form copper resinates or linoleates which, in turn, can produce copperstained films. On the other hand, Rees Jones (1965) stated that in European paintings a common device for obtaining a green of increased saturation was to glaze with transparent copper resinate (see chapter 6) over malachite or malachite mixed with yellow. Either variation in painting practice could explain why such films sometimes give diffuse x-ray diffraction patterns that are difficult to interpret. The Japanese painters, however, had no such problem; they employed coarsely ground malachite to represent the deep green of foliage and a more finely ground pigment for the bright green of costumes (see figs. 2 and

Malachite is found abundantly used with azurite in Western Chinese paintings of the ninth to tenth centuries at Dun-huang (Waley, 1931) and in other central Asian sites. It has been identified in wall paintings of Ming times in Central China (Gettens, 1938). Yamasaki (1953 and 1967) reported it as occurring in the seventh- to eighth-century Buddhist wall paintings of the Hōryūji Temple near Nara in Japan, and it was abundantly used in scroll and screen paintings in Japan up to and including the present century (fig. 2).

In European easel painting, malachite seems to have been of importance mainly in the fifteenth and sixteenth centuries in both egg tempera and oil-medium, undergoing some minor revival in the nineteenth century. It is quite suitable for the technique of true fresco.

In classical and medieval writings, what we now call malachite was referred to as "chrysocolla," a word derived from the Greek χουσοζ (gold) and κολλα (glue) because it was used by the ancients in soldering gold. Augusti (1959 and 1967), in his fine monograph on Pompeiian pigments, devoted a long passage to the mention of chrysocolla by various classical writers—Theophrastus, Vitruvius, Pliny, and others. The term chrysocolla was later given by mineralogists to the blue-green natural cryptocrystalline hydrosilicate of copper of indefinite composition (see below). Harley (1982, pp. 77–78) discussed the confusion in terminology in some detail. There is an interesting footnote in the Hoover and Hoover (1950) translation of Agricola's De Re Metallica (footnote 15, p. 584) that merits attention: Agricola (De Natura Fossilium, p. 215) in discussing sub-



Fig. 2 An example of the use of malachite on a Japanese panel painting on silk. Portrait of Sato Issai, Edo Period. Nanga school, by Watanabe Kazan (1793–1841). Courtesy Freer Gallery of Art, No. 68.66. Photo: Raymond A. Schwartz.

stances, which originate from copper, gives among them green chrysocolla (as distinguished from borax, etc., see Church, 1890). Agricola wrote:

Native *chrysocolla* originates in veins and veinlets, and is found mostly by itself like sand, or adhering to metallic substances, and when scraped off from this appears similar to its own sand. Occasionally it is so thin that very little can be scraped off. Or else it occurs in waters



Fig. 3 Malachite mineral ground to various grades of fineness resulting in pigment brightness ranging from light to medium to dark. Produced by Ishida Hōkōdō Co. of Kyoto, Japan. Photo: Raymond A. Schwartz.

which, as I have said, wash these minerals, and afterward it settles as a powder. At Neusohl in the Carpathians, green water flowing from an ancient tunnel wears away this *chrysocolla* with it. The water is collected in thirty large reservoirs, where it deposits the *chrysocolla* as a sediment, which they collect every year and sell [as a pigment].

This description of its occurrence would apply equally well to modern chrysocolla or to malachite. The solution from copper ores would deposit some sort of green incrustation, mostly of carbonates.

Preparation

Selected lumps of malachite were crushed, ground to a powder, washed, and levigated to prepare it for pigment use. In the Ishida Hōkōdō colorman's shop in Kyoto, Japan, one of the authors (Gettens) observed a workman levigating ground malachite by swirling it with water in a large ceramic tray. In this shop it was produced in various grades, but principally coarse, medium, and fine (fig. 3), which produced corresponding dark, medium, and light tones of green paint when used with aqueous medium. Particle sizes were measured on three of the "fineness grades" of the pigment malachite supplied by the Ishida Hōkōdō shop. The particles of the "coarse" grade ranged from 40 to 160 μ with 75% being 80–120 μ ; the "medium" particles ranged from 4 to 54 μ , 66% being 4–14 μ; the particles of the "fine" grade ranged from 1 to 11 μ , with 92% being 1–5 μ . The dimension measured was Feret's diameter, which is the distance between imaginary parallel lines tangent to the particle profile and perpendicular to the ocular scale.

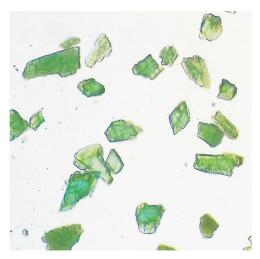


Fig. 4 Coarse malachite, Japanese pigment (rokusho) obtained from Y. Yashiro in Japan in 1931 by Edward W. Forbes for the Fogg Art Museum, 121x. Mounted in Canada balsam.

A. In transmitted light.

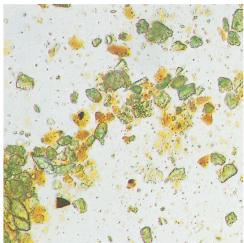
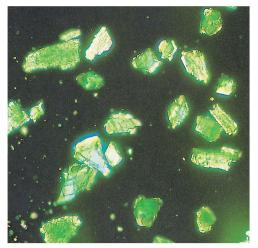
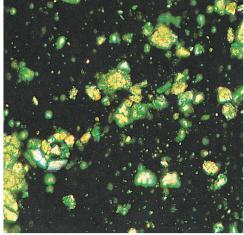


Fig. 5 Malachite from a Madonna by a follower of Antoniazzo Romano, School of Rome, late fifteenth or early sixteenth century. Walters Art Gallery, Baltimore, No. 37.703. Mounted in Canada balsam. A. Transmitted light, 298x.



B. Same field in crossed polars.



B. The same field between crossed polars.

Particle Characteristics

As seen in figure 1, malachite often occurs in large botryoidal (rounded) masses with a fine fibrous structure. A special characteristic of massive malachite is color banding ranging from near black to pale green. Banding is a feature found in several minerals, which are deposited from solutions. Vestiges of banding may sometimes be observed in coarse pigment particles (fig. 6). Because the pigment is produced by crushing and grinding, all the particles have a fractured appearance (fig. 7), which is described by Dana as "subconchoidal to uneven" (Palache, 1951). Many of the larger particles have a definite fibrous structure (figs. 4 and 5). Also, it is not uncommon to find particles of the associated minerals: azurite, chrysocolla, and cuprite, mixed with malachite (see below).

The specific gravity is about 4.0; hardness is $3\frac{1}{2}-4$.

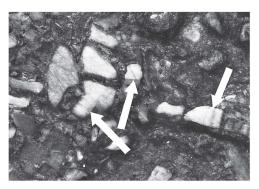


Fig. 6 Coarse particles of malachite in the artificial patina of an ancient Chinese bronze ceremonial vessel of the type *huo*. Freer Gallery of Art, No. 09.254. The banding, characteristic of malachite, shows plainly (arrows), 15x.

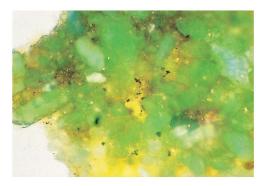


Fig. 7 Top surface of a fragment of paint from the landscape in Perugino's *Virgin and Child with Saint John*, panel, c.1500. National Gallery, London, No. 181. The characteristic angular particle form of ground natural malachite is evident (compare fig. 13). Reflected light, 473x. Photo: A. Roy.

Optical Properties

In transmitted light, even the coarser particles are quite pale green, but they show high relief and dark edges (figs. 4 and 5), especially when mounted in a medium of much lower refractive index such as Canada balsam or Aroclor. The finer particles are nearly colorless; the coarser particles show noticeable pleochroism varying from nearly colorless to green (figs. 4 and 5). Malachite belongs to the monoclinic crystal system: $\alpha = 1.655$, $\beta = 1.875$, $\gamma = 1.909$. Twinning is common.

Chemical Properties

Like azurite, malachite is stable to light and normal atmosphere. The finely powdered material is slowly darkened by hydrogen sulfide. When heated at a slow rate, finely divided malachite loses weight by loss of water beginning at about 200°C, and at 600°C decomposition is nearly complete. Carbon dioxide is also given off and the black residue is cupric oxide (CuO, tenorite) (Simpson et al., 1964). Malachite is unaffected by cold dilute sodium hydroxide, but blackens when warmed in that reagent; it is decomposed by dilute acids, even acetic acid, with release of bubbles of carbon dioxide gas, but when mixed with organic medium, the gas release may be quite slow. When small specimens are treated on a microscope slide with dilute hydrochloric acid, a ring of orangebrown needlelike crystals of cupric chloride is formed on drying; with dilute nitric acid, pale green crystals of cupric nitrate remain. With the acid reagents, abundant Cu2+ ions are formed that are easily identified by microchemical tests.

Permanence

Malachite is moderately permanent. It is unaffected by strong light, and even though theoretically subject to blackening when mixed with sulfide pigments, in practice, darkening from this cause apparently has not been reported. The malachite areas on medieval Italian frescoes are often still fairly bright green.

Microchemical Tests

The microchemical tests for copper, already described by Gettens and FitzHugh for that element in azurite, which include the ferrocyanide, the triple nitrite, and the potassium mercuric thiocyanate tests, are equally applicable to malachite (see chapter 1). The advantage of the ferrocyanide test is that it can be used to identify copper in a single particle of malachite (chapter 1, fig. 8).

Spot Tests

The tests described for copper in azurite (see chapter 1) are equally applicable to malachite.

Criteria for Positive Identification

Malachite is ordinarily quite easy to identify by microscopic and microchemical methods. Chief diagnostic features are: the pale greenish color of the particles by transmitted light (except the smallest and thinnest particles, which are practically colorless); the fibrous nature of some of the larger particles; high birefringence; solubility in

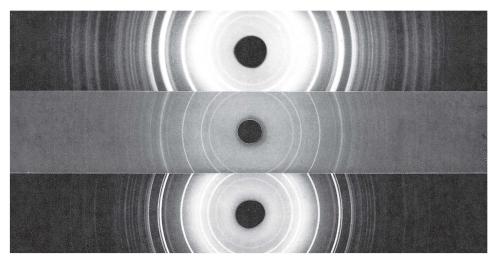


Fig. 8 X-ray diffraction powder patterns of malachite.

A. Malachite mineral. Bisbee, Arizona. Department of Mineral Sciences, Smithsonian Institution collection.

B. Malachite pigment. Japanese painting, style of Sotatsu, Momoyama-Edo, Rimpa School, early

seventeenth century. Freer Gallery of Art, No. 03.101. C. Copper carbonate. Eimer & Amend. Photographs not to be used for measurement purposes. XRD patterns by Elisabeth West FitzHugh.

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dilute acids with possible evolution of gas bubbles; and a positive test for copper. It is impracticable to attempt identification of evolved carbon dioxide gas in microscopic-sized samples. Confirmation of the mineral species is most easily done by x-ray diffraction analysis, although natural and artificial varieties may not be distinguished by this means. Other instrumental methods described below may be preferred in some cases. X-ray fluorescence analysis for the detection of copper can be applied equally to malachite and azurite (see chapter 1). Green color of paint and a positive test for copper are not sufficiently diagnostic as these would be exhibited by emerald green, verdigris, copper resinate, and others.

Emission Spectrographic Analysis

Copper in malachite may be detected spectrometrically by the same spectral lines used for detecting copper in azurite. Prominent lines in the visible range are: 5218.20, 5153.23, and 5105.54 Å; in the ultraviolet they are: 3274.0, 3247.5, and 2824.4 Å; sensitivity is 0.0001% (Waring & Annell, 1953). In the spark spectrum, an emission line at 2247.0 Å may be used for copper.

X-ray Diffraction Analysis

Malachite gives a strong x-ray diffraction powder pattern. The *d* spacings and intensities of a sample of malachite recrystallized from reagent grade basic copper carbonate and carbonic acid in a Morey bomb at 300°C, measured at the U.S. National Bureau of Standards, are shown in table 1 (*JCPDS Powder Diffraction File*, 1963). X-ray diffraction patterns for malachite from three different sources are shown in figure 8.

Color and Spectral Reflectance

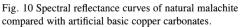
Malachite has only fair hiding power in oil paints but produces a moderate green when mixed with aqueous media such as animal glue. Its masstone hue varies from a green equivalent to Munsell 6G to a bluish green of about 3.5 BG. The dominant wavelength, which may vary from 495 to 515 nm, is not markedly changed by mixture with white. Measurements on the color of a number of samples of malachite, summarized in table 2, include materials that are synthetically prepared basic copper carbonate and the three samples of natural malachite (*rokusho*) from Ishida Hōkōdō, Kyoto, described above. The earlier data of Barnes (1939) are also included.

The spectral reflectance of several of the samples is shown in figures 9 and 10. The very

Table 1 X-ray Diffraction Data for Malachite^a

d(Å)	I	$d(\mathring{A})$	1
7.41	12	1.899	14
5.993	55	1.855	4
5.055	75	1.833	10
4.699	14	1.790	12
		1.696	10
3.693	85		
3.028	18	1.691	25
2.988	18	1.678	14
2.857	100	1.640	12
2.823	40	1.616	18
		1.589	18
2.778	45		
2.520	55	1.571	14
2.477	30	1.541	8
2.464	35	1.531	14
2.425	20	1.498	14
2.349	14		
2.316	18	1.476	18
2.289	18	1.472	12
2.252	8	1.422	8
2.186	20	1.418	16
2.100	20	1.406	6
2.160	8	11100	Ü
2.129	20	1.386	10
2.076	18	1.362	4
2.054	10	1.352	10
2.022	6	1.349	12
1.991	12		
1.969	18		
1.969	16		
1.947	10		
1.941	18		
1.711	10		

a. JCPDS Powder Diffraction File 10–399 (synthetic malachite). Diffractometer, $CuK\alpha$ radiation, Ni filter. (Courtesy of JCPDS International Centre for Diffraction Data.)



A. Basic copper carbonate, Baker Chemical Co., with TiO,.

Courtesy R. L. Feller and Mary Curran, National Gallery of Art Research Project, Carnegie-Mellon University, Pittsburgh.

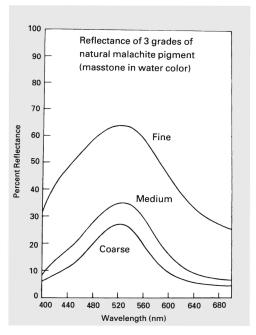
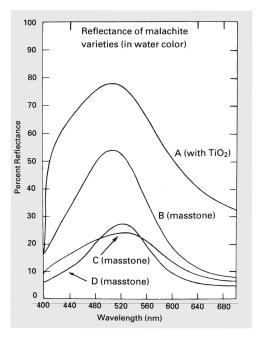


Fig. 9 Spectral reflectance curves of fine, medium, and coarse malachite painted out in thin animal glue (nikawa) medium. Pigment from Ishida Hōkōdō Co., Kyoto. Courtesy R. L. Feller and Mary Curran, National Gallery of Art Research Project, Carnegie-Mellon University, Pittsburgh.



B. Same, without admixture of white.

C. Basic copper carbonate, Fisher Scientific Co.

D. Natural malachite pigment, coarse, from Ishida Hōkōdō Co., Kyoto, Japan.

Table 2 Measurements on the Color of Malachite

	CIE Tristimulus Coordinates, Illum.Ca					
	х	у	Υ	L*	a*	<i>b</i> *
Natural (Barnes, 1939)	0.2924	0.3493	41.77	70.71	-15.46	2.913
Fisher Basic Copper Carbonate	0.2695	0.3470	18.98	50.66	-18.68	-0.5975
Same plus Titanium White	0.2903	0.3301	50.13	76.15	-10.11	-2.954
Baker Basic Copper Carbonate	0.2379	0.3370	35.61	66.22	-33.42	-7.158
Same plus Titanium White	0.2768	0.3232	65.23	84.6	- 14.76	-7.605
Natural Malachite (A	Rokusho)					
(coarse)	0.2562	0.3912	18.34	49.91	-33.14	6.915
(medium)	0.2681	0.3767	24.91	56.99	-28.89	5.867
(fine)	0.2868	0.3400	55.53	79.35	-15.99	-0.4779
Malachite (Rokusho)					
plus Lead White	0.2942	0.3338	54.44	78.72	-10.10	-1.306

a. Data only available for illuminant C. Although CIE standard illuminant D65 is commonly used, it is close to illuminant C on the chromaticity diagram. Calculation of L^* , a^* , b^* values by David Saunders.

slight dip in the curve at about 440–450 nm seems to be a characteristic, for it appears also in Barnes' curve as well as in nearly all of the samples measured in the present investigation. The sharp rise from 400 to 420 nm may also be characteristic, although this part of the curve is influenced by the white mixed with the green. The location of the maximum in the reflectance curves is not characteristic but may vary from about 505 nm in the bluish green samples to perhaps 525 nm in the green. This is because the color of malachite, as with many similar copper compounds, is based on two principal absorption, not reflectance, phenomena. Tetragonal distortion of the octahedral crystal field gives rise to four energy levels, and for the d⁹ (Cu²⁺) configuration, three electronic transitions become possible, although the absorption bands overlap to produce a single broad peak in the red and near infrared (Patterson, 1967). Absorption in the violet or ultraviolet results from "charge transfer" from the ligand to the metal. Variations in the color of basic copper salts can be influenced by variations in the other anions that are present, such as the carbonate or halides that influence particularly the charge-transfer band

that occurs at the shorter wavelengths. Kühn, for example, reported the maximum reflectance to vary from 485–545 nm for verdigris and copper resinate (see chapter 6). Rees Jones (1965) discussed the effect on the color of malachite when it is mixed with buckthorn and with massicot. He further indicated (p. 75) that malachite mixed with yellow for green is frequently found in Early Netherlandish and Flemish paintings as well as being mentioned by Cennino Cennini. Combinations with lead–tin yellow are most likely to have been used.

Infrared and Raman Spectra for Malachite

The infrared spectrum of malachite was published by Sadtler (*Sadtler Midget Edition*, n.d.), Nyquist and Kagel (1971), Flieder (1969), and Kühn (1964). Goldsmith and Ross (1968) published a normal coordinate analysis for natural malachite and derived assignments for the bands. As shown in figure 11, the spectrum is characterized by a broad carbonate absorption between 1400 and 1500 cm⁻¹ and a hydroxyl function at 3400 cm⁻¹.

Table 2 Continued

	Data Derived from Tristimulus Values			
	Dominant Wavelength Nanometers	Purity %	Approx: Munsell Notation	ISCC-NBS Standard Color Name
Natural (Barnes, 1939)	515.2	6.6	6G/6.9/3.4	Light green
Fisher Basic Copper Carbonate	500.2	13.5	10G/4.9/4	Moderate bluish green
Same plus Titanium White	499.5	6.5	2BG/7.5/2.5	Light bluish green
Baker Basic Copper Carbonate	495	22	3.5BG/6.5/7	Light bluish green
Same plus Titanium White	493	12	6.5BG/8.3/3.6	Very light bluish green
Natural Malachite (Rok	usho)			
(coarse)	509	18	6G/4.8/7	Moderate green
(medium)	510	14	6.5G/5.5/6.4	Moderate to light green
(fine)	504	7.2	8.8G/7.8/3.6	Very light green
Malachite (Rokusho)				
plus Lead White	509	5.0	8.5G/7.7/2.4	Very pale green

Very strong carbonate stretching bands occur at 1500 and 1400 cm⁻¹, and also contribute medium-intensity absorptions at 1095, 820, and 748 cm⁻¹; weaker features occur at 1800, 803, and 710 cm⁻¹. O-H bending modes produce two peaks, a strong absorption at 1045 cm⁻¹ and a medium-intensity absorption at 875 cm⁻¹. Below 600 cm⁻¹ the copper–oxygen skeleton shows stretching absorptions at 570-580, 522, 505, 425, and 337 cm⁻¹, and bending mode bands at 325, 295, 278, 206, 176, 152, and 132 cm⁻¹. The infrared spectrum is more complex in this region than it is for azurite. The curves given by Flieder and by Nyquist and Kagel show an absorption band at 3300 cm⁻¹ that is not seen in the Sadtler spectrum or in two samples of synthetic basic copper carbonate examined. This band may be caused by absorbed water.

The relative intensities of the bands at 820 cm⁻¹ and 875 cm⁻¹ vary in different samples. Although the band of lower wave number possesses the greater absorption in the three published curves cited, it is less intense in the natural mineral from Ishida Hōkōdō, Kyoto (fig. 11, upper curve). The

latter sample contains traces of ochrelike impurities, and the spectrum of this natural malachite is given so that the slight variations in the spectrum can be seen. The double band at 3590 cm⁻¹ is characteristic of kaolinite and hydrated halloysite minerals. Bands at 1120 and 780 cm⁻¹ may be caused by the ochrelike impurity. The differences in the curves between 3200 and 1800 cm⁻¹ may be encountered in various samples and arise because of scattering, which is most intense in the upper curve and least in the middle one.

Infrared spectra in the range 3950–450 cm⁻¹ have also been recorded for malachite (and azurite) using the new technique of photothermal beam deflection spectroscopy (Low & Tascon, 1985).

Guineau (1984) published the Raman spectrum of malachite for a Forbes collection reference specimen and discussed the use of the laser Raman microprobe for the nondestructive detection of malachite and azurite on small fragile objects. The principal Raman active vibrations for malachite are at 1498, 1104, 1060, 540, 437, 355, 274, and 225 cm⁻¹.

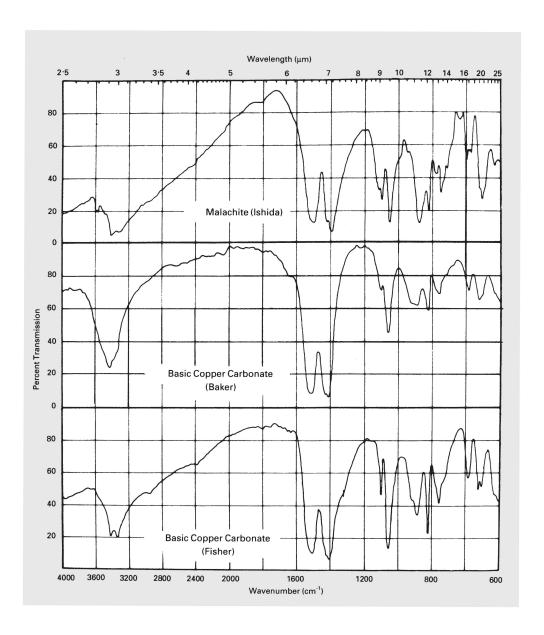


Fig. 11 Infrared absorption curves for malachite and artificial basic copper carbonates. *Upper*: malachite pigment; medium grade, supplied by Ishida Hōkōdō Co., Kyoto. (KBr pellet): *Middle*: artificial basic copper carbonate, Baker Chemical Co. (KBr pellet);

Bottom: artificial basic copper carbonate, Fisher Scientific Co. (600–1320 cm⁻¹ Nujol mull; 1320–4000 cm⁻¹ halocarbon mull). Courtesy F. R. Dollish and G. L. Carlson. Research Services Department, Carnegie-Mellon University, Pittsburgh.

Neutron Activation Analysis

The use of this method of analysis to identify trace elements in azurite would also apply to malachite (see chapter 1).

X-radiography

Like azurite, areas of paintings painted with malachite show only moderate opacity to x-rays (Rees Jones, 1975). De Wild (1929) gives the mass absorption coefficient (μ /c) of malachite using wavelength 0.708 Å as 27.0 as compared with azurite, 26.0.

Sayre and Lechtman (1968) showed that when copper pigments including malachite are irradiated with thermal neutrons in an atomic reactor, they produce two copper radio-isotopes with sufficiently short half-lives to lend themselves to autoradiography. One is ⁶⁶Cu with a half-life of 5.1 minutes that emits high-energy beta (2.6 MeV); the other is ⁶⁴Cu with a half-life of 12.8 hours that emits a relatively low-energy beta (0.57 MeV), and low-energy positron (0.65 MeV).

Chrysocolla and Other Associated Minerals

In addition to the azurite mentioned above, malachite is associated in nature with cuprite (Cu₂O), a red mineral, and also, at times, with blue-green copper silicate that modern mineralogists call chrysocolla. This is a nearly amorphous mineral that is in the nature of a solidified hydrogel with a cryptocrystalline phase. The refractive index varies from 1.45 to 1.55. All grains show aggregate polarization. In dilute hydrochloric acid, the color is leached out leaving the form of the grains unchanged. Some of the leached grains are isotropic, but most are anisotropic with low birefringence. The anisotropic grains show aggregate, undulating, and flamboyant extinction. Many grains show banded, fibrous, microspherulitic, and microglobular structure. In the older texts the chemical formula is given as CuSiO₃.2H₂O, but according to Sun Ming-Shan (1963), from whom much of this information is taken, this formula is much questioned and should only be considered as an approximation. Most samples of chrysocolla give diffuse and sparse x-ray diffraction patterns, much like silica gel or other amorphous materials. The spacings and intensities in table 3, measured on the cryptocrystalline phase of a sample from the Inspiration Mine, Miami, Arizona, were given by Sun Ming-Shan (p. 653), with a distinct crystal-

Table 3 X-ray Diffraction Data for Chrysocolla

(Radiation CuK $\alpha = 1.5418 \text{ Å}$)

(a) Data: Sun Ming-Shan (1963, p.653)

d(Å)		Ι	d(Å)		I
15.0 4.39	(dark halo) (diffuse)	10	2.42	(diffuse) (diffuse)	
2.77 }	(wide band)		1.505)	,	
$2.51 \ 2.62$	(wide band)	4	1.482 1.321	(diffuse) 8 (diffuse) 2	

(b) Data: JCPDS Powder Diffraction File 27-188

$d(\mathring{\mathbf{A}})$	I	d(Å)	
17.9	8	2.90	8
7.9	6	2.56	7
4.45	2	1.602	4
4.07	6	1.406	10

line species reported (1970) to the *JCPDS Powder Diffraction File* (table 3).

Chrysocolla has been found occasionally as a pigment material, mostly on ancient Asian wall paintings (Bontinck, 1945; Gettens, 1938a and 1938b). Identifications can be questioned unless based on detailed criteria. Although a bluer green than malachite, chrysocolla could be either a substitute or an impurity.

The basic chlorides of copper, both atacamite and paratacamite, can occur as impurities, corrosion products in, or even as substitutes for malachite. In the wall paintings of the fourteenth-century church in Istanbul, now known as the Kariye Camii, patches of bright green in areas of blue sky were identified as paratacamite (Gettens & Stout, 1958). Similar phenomena have been noted in Austrian wall paintings of the thirteenth to fifteenth centuries (Kerber et al., 1972). It was thought to be a corrosion product formed by action of common salt (NaCl) in the plaster on the azurite pigment originally used to represent the blue vault of heaven. Hence, the basic copper chlorides may also serve to confound the analyst in the identification of copper green pigments.

Verditer and Other Artificial Copper Greens

Artificial basic copper carbonate greens, sometimes called green verditer (derived from vert de terre) or green bice, are mentioned in the seventeenth-century literature but do not seem as widely used as blue verditer (see chapter 1). Harley (1982) notes a late-sixteenth-century price list that includes the pigment. Laurie (1914) mentioned both blue and green verditer and indicated that the verditers were made by pouring copper nitrate solution onto whiting (calcium carbonate) after which the pigment was drained, washed, and dried. It was inexpensive to make, but apparently it was too pale in color for practical use so that by the eighteenth century it seems to have disappeared from the artist's palette. No samples of authentic green verditer are available at present for precise description of particle or optical characteristics, although some early examples of what appears to be artificial malachite have been reported (Smith et al., 1981; Braham et al., 1978; Wyld & Plesters, 1977; Bomford & Kirby, 1978; Van Os et al., 1978). In several quattrocento panel paintings in the National Gallery, London, a green globular pigment has been detected that shows an x-ray diffraction (XRD) pattern identical to that of natural malachite but a particle morphology consistent with a precipitated origin (see fig. 12 and Notable Occurrences) (Smith et al., 1981). Mühlethaler described the making of artificial malachite from CuSO₄.5H₂O and Na₂CO₃. The x-ray diffraction pattern of his synthetic material agrees well with that of the natural mineral. He also showed transmission electron micrographs of the synthetic malachite at 12,000x (Schweizer & Mühlethaler, 1968). Artificial basic copper carbonates are available from scientific supply houses. Because of their small particle size, they are pale green (fig. 13). An interesting feature is that the particles are spherulitic in shape and, hence, show a black cross when viewed in crossed polars (fig. 14). The color reflectance and infrared spectra of two of them have been measured and compared with natural malachite pigment (table 2 and figs. 10 and 11). Scanning electron micrographs show definite differences in particle characteristics between natural malachite and artificial basic copper carbonate and between different forms of the artificial variety (fig. 15A–E). There is also the possibility that other artificial copper basic salts may be identified in paintings. In a nineteenth-century German collection of pigments and painting materials described by Richter (1972) of Stuttgart, a green pigment powder was identified as basic copper sulfate. Similarly, a sample of powdered artificial green supplied from old stocks by an English colorman to Joyce

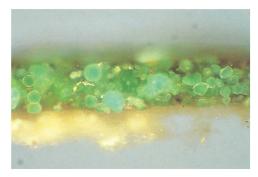


Fig. 12 Paint cross section from the dark green foreground paint in Francesco del Cossa's *Saint Vincent Ferrer*(?), panel, c.1472. National Gallery, London, No. 597. The pigment has been identified by x-ray diffraction as malachite, but the globular particle form suggests artificial preparation by precipitation (see also fig. 16C). Reflected light, 473x. Photo: A. Roy.

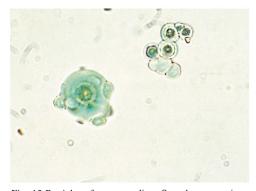


Fig. 13 Particles of green verditer. Sample preparation by P. Mactaggart, No. 1514. Transmitted light, 682x.

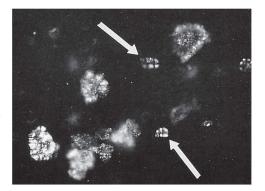


Fig. 14 Basic copper carbonate, Fisher Scientific Co., in crossed polars, showing characteristic spherulitic particles (arrows). Mounted in Canada balsam, 623x.

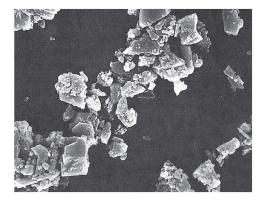
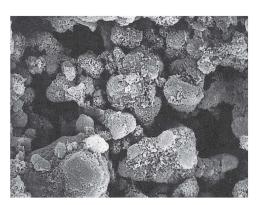
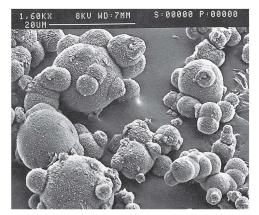


Fig. 15 Scanning electron micrographs of malachite and artificial malachite.

A. Natural malachite, printed at 2,130x.

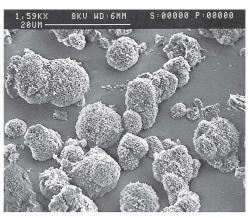


B. Artificial basic copper carbonate, Fisher Scientific Co., printed at 2,130x.



C. Artificial basic copper carbonate, P. Mactaggart, No. 1514 (see fig. 13). Gold-coated, printed at 1,136x.

Photos A–B courtesy of John Winter, Freer Gallery of Art and Walter R. Brown, National Museum of Natural History, Smithsonian Institution. Photos C–F by A. Roy.



D. Artificial basic copper carbonate, P. Mactaggart, No. 1615. Gold-coated, printed at 1,129x.



E. Specimen as D, detail printed at 4,260x.



F. Nineteenth-century Winsor & Newton sample labeled "malachite." Shown by x-ray diffraction actually to be brochantite (artificial basic copper sulfate). Gold-coated, printed at 4,459x.

Plesters was found to give an x-ray powder pattern of brochantite (basic copper sulfate) (fig. 15F). Several different basic copper salts have been found as green pigments in a variety of objects other than easel paintings (Van't Hul-Ehrnreich & Hallebeek, 1972), including basic copper nitrate, basic copper phosphate, and basic copper chloride (see also Richter, 1988). A variety of both natural and artificial green copper compounds have also

been identified on Russian wall paintings from the sixteenth century onward, including malachite, atacamite, posnjakite (a basic copper sulfate), and natural pseudo-malachite (a basic copper phosphate) (Naumova et al., 1990). Church (1890) treated malachite as a nineteenth-century pigment and reported it was sometimes adulterated with baryta white (BaSO₄) and fortified with arsenical green.

Notable Occurrences

Malachite—in Western Paintings

Date	Artist/School, Title, Description, Collection or Location	Analyst and Method of Identification
1st C	Roman Nero's Golden House (painted plasterwork), British Museum, London	A. Roy, XRD
2nd C	Pompeii Crystalline powder, National Museum, Naples, No. 111/17364/Na.	S. Augusti (1967), micr.
700–1500	European Illuminated medieval manuscripts	A. P. Laurie (1914), visual inspection
11th–16th C	European Eight illuminated manuscripts, Paris, Bibliothèque Nationale and Archives Nationales	F. Flieder (1968), micr.
14th/15th C Italian	Attributed to Spinello Aretino Madonna and Child Enthroned with Angels, Fogg Art Museum, 1905.1	R. J. Gettens (1947), micr.
15th/16th C Italian	Girolamo di Benvenuto Madonna Enthroned with Saints and Angels, Fogg Art Museum, 1927.206	R. J. Gettens (1935), micr.
1420-1460 Polish	"Cracow School" Eight paintings	J. Nykiel (1969), micr.
c.1432	Jan van Eyck The Mystic Lamb Altarpiece, Cathedral of St. Bavon, Ghent	P. Coremans and J. Thissen (1953), micr.
1450–1800	Six paintings mainly by Flemish Masters Dutch Museums and private collections	A. M. de Wild (1929), micr.
late 15th C	North Netherlandish Polychrome sculpture	C. M. Groen (1978), micr.

XRD = X-ray diffraction

micr. = Identification with the microscope

Date	Artist/School, Title, Description, Collection or Location	Analyst and Method of Identification
late 15th/early 16th C Italian	Follower of Antoniazzo Romano, School of Rome Madonna and Child, Walters Art Gallery, 37.703	E. W. FitzHugh, micr. (see fig. 6)
1560-1562 Italian	Tintoretto The Last Judgment, Church of the Madonna dell'Orto, Venice	J. Plesters, micr., private communication
1882 French	Pierre Auguste Renoir Oil painting <i>Chrysanthemums</i> , Art Institute of Chicago, 1933.1173	M. Butler, micr.

Malachite in Easel Paintings in the National Gallery, London

Date	Artist and Title	Acquisition Number
Malachite of s	pherulitic particle form, probably artificial ^a	
1437–1444	Stefano di Giovanni, known as Sassetta The Whim of the Young St. Francis to Become a Soldier (panel from an alterpiece) (Wyld & Plesters, 1977)	4757
mid-15th C	Cosimo Tura An Allegorical Figure (Dunkerton et al., 1987)	3070
1460s	Giovanni Bellini The Blood of the Redeemer (Braham et al., 1978)	1233
1460s	Giovanni Bellini The Agony in the Garden	726
c.1473	Francesco del Cossa St. Vincent Ferrer (Smith et al., 1981) (see fig. 13)	597
3rd quarter 15th C(?)	Giovanni di Paolo Sts. Fabian and Sebastian (Bomford & Kirby, 1978)	3402
Malachite of n	nineral particle form ^b	
c.1300	Duccio The Virgin and Child with Four Angels	6386
2nd quarter 15th C	Piero della Francesca The Baptism of Christ	665
late 15th C	Perugino The Virgin and Child (see fig. 8)	181
1504	Cima da Conegliano The Incredulity of St. Thomas (Dunkerton & Roy, 1986)	816
1517–1519	Sebastiano del Piombo The Resurrection of Lazarus	1

a. In all cases, the medium of painting was shown by gas chromatography to be egg. Confirmation of basic copper carbonate by x-ray diffraction.

b. The pigment was identified by chemical methods (tests for Cu^{2+} and occasionally CO_3^{2-} ions), microscopical methods (particle characteristics, double refraction, refractive index measurement) and spectrographic analysis (laser microprobe) in the Scientific Department of the National Gallery, London, by Joyce Plesters and Ashok Roy.

Date	Artist and Title	Acquisition Number
c.1540-1550	Bronzino An Allegory	651
1556	Tintoretto Christ Washing His Disciples' Feet (Plesters, 1980)	1130
1560s	Tintoretto St. George and the Dragon (Plesters, 1980)	16
1st quarter 17th C	Domenichino Apollo Pursuing Daphne ^c	6287

c. This is one of a series of transferred frescoes, originally painted for the Villa Aldobrandini at Frascati; visual comparison strongly suggests that malachite is the predominant green pigment in the other frescoes of the series (National Gallery Nos. 6284–85 and 6288–91).

Malachite Reported by Hermann Kühn, Munich

Date	Artist/Country, Title or Object	Collection or Location
3rd C B.C.	Egyptian Two mummy masks, painted textile	Staatlich Sammlungen Agyptischer Kunst, Munich
3rd C B.C.	Greek Eight grave stelae	Archaeological Museum, Volos, Greece
с.200 в.с.	Egyptian Bird, painted and gilded wood sculpture	Staatlich Sammlungen Agyptischer Kunst, Munich, Inv.No.1350
2nd C в.с.	Greek (Sicilian) Centurip Winged Female Head painted terra-cotta sculpture	Staatlich Antikensammlungen, Munich, Inv.No.5016
1025/1028	German, late Ottonian wall painting	Cathedral of Verden, Aller, Germany
1st quarter 12th C	German, wall painting in old choir	Church of Kappel (Oberschwaben)
e.1160/1170	German, wall painting	Karner of Perschen Oberfalz
14th C	Swiss, wall painting	Church of Aeschi
15th C	Hugo van der Goes Madonna and Child Lenten altar cloth	Bavarian State Collection, BSTG Inv.No.L821
15th C	Master of the Epitaph of Florian Winkler Epitaph of Florian Winkler wood panel	Städtich Museum, Wiener Neustadt, Austria
1440	German, wall painting	Parish Church of Linden, Oberbayers
1484–1490, 1499, c.1560	German, wall paintings	Sachsen Cathedral, Freiberg
1497	Michael or Gregor Erhard Moerlin-Epitaph, sandstone sculpture	Schaezler-Palace, Augsburg

Date	Artist/Country, Title or Object	Collection or Location
(?)	Raphael The Holy Family from the Casa Canigiani	BSTG Inv.No.476
c.1515	Austrian Wing of an altarpiece	Parish Church of Ossiach, Kärnten, Austria
1517/1518	Veit Stoss Angelical Salutation, lindenwood sculpture	St. Lorenz Church, Nuremberg
2nd half 16th C	German Wall painting	Andreas Chapel of Bamberg Cathedral
18th C	German Basket of Flowers parchment on walnut panel	BSTG Inv.No.7072
1730–1731	Johann Baptist Zimmerman Fresco in cupola and polychromy of stucco	Pilgrim Church Sts. Peter and Paul, Steinhausen near Schussenried, Germany

Malachite in Far Eastern Objects and Paintings

Date	Artist/Country, Title, Description, Collection or Location	Analyst and Method of Identification
7th–8th C	Japan Buddhist wall paintings, Hōryūji Temple	K. Yamasaki (1953; 1967)
10th C	Japan Four Lokapalas, painted wooden plaques, Ninnaji Temple, Kyoto	Y. Emoto (1968) XRF
Sung and Ming Dynasties	In false (painted) patina Several archaistic Chinese ceremonial bronze vessels, Freer Gallery of Art	R. J. Gettens (1969) micr.
14th C	Japan Ten wooden panels, sacred figures, Rinnuji Temple, Nikko	T. Nakazato and S. Tatsuta (1971) XRF
1551	China, Shansi Wall painting, <i>Vision of Kuan Yin</i> , Museum of Fine Arts, Boston	R. J. Gettens (1938b) micr.
late 16th–mid- 19th C	Japanese artists of the Ukiyo-e School eighty paintings, Freer Gallery of Art	E. W. FitzHugh (1979) micr.

Malachite in the Western Hemisphere

pre-Columbian	Guatemala Various objects	A. O. Shepard (1946), micr.

BSTG = Bayerische Staatsgemäldesammlungen, Munich

micr. = Identification by the microscope

XRF = X-ray fluorescence

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Calcium Carbonate Whites

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Introduction

Calcium carbonate in various forms has had from earliest times a wide role in art. The most common natural form of calcium carbonate is calcite. It is ubiquitous in the mineral, animal, and vegetable kingdoms. It occurs mainly in sedimentary rocks such as chalk and limestone, but it is also in metamorphic rocks such as marble and even occasionally in igneous rocks. Calcite (and sometimes its dimorph, aragonite) is the main constituent of some mollusc shells, but living or fossil lower organisms of recent origin are more likely to be composed of aragonite, the less stable form, which is converted to calcite with changes in environment, particularly heating (Palache et al., 1951). Calcite also occurs as the skeletal material of many forms of marine life, such as the Foraminifera and Coccolithophoridae. It is the main constituent of cave deposits, onyx marble, and other concretionary lime carbonate rocks. Pure calcium carbonate is white; hence, it has many uses in powdered as well as in massive forms in arts and industries. The powdered whites are still used as the principal pigment white in some modern paints and as extenders and bulking agents for white hiding and colored paints. The different types of calcium carbonate pigments that have a place in the history of painting materials are calcite, chalk, precipitated chalk, lime white, shell white, and coral. They are differentiated mainly by particle characteristics, which will be described for each kind. First, we shall consider the general aspects of each variety.

Calcite, Marble, and Limestone

English: calcite German: Kalzit (m.) French: calcite (f.) Italian: calcite Spanish: calcita Russian: Кальчит

English: marble German: Marmor (m.) French: marbre (m.) Italian: marmo (m.) Spanish: marmol Russian: Мрамор

Calcite is the name given by mineralogists to the most common mineral form of calcium carbonate, CaCO₃. Two less common polymorphic forms are aragonite and vaterite. Calcite commonly occurs in large single transparent crystals. There are massive types, from coarse granular to impalpable. An especially pure variety is called Iceland spar. Marble is metamorphosed limestone that is recrystallized calcite in which the calcite grain size may be fairly coarse as in lump sugar, but the name may be applied to any lime carbonate rock that is capable of taking a polish. Some concretionary calcite is quite finely crystalline.

All these forms of calcite may be found in paintings, in the pictorial layers as well as in the support structures, along with varying amounts of common impurities, which may include quartz, magnesite, dolomite, clays, and coloring agents such as haematite, carbon, and others. Ground marble or marble dust was used in fresco painting. In America, where there is little high-quality chalk, ground limestone often serves as a source

of natural calcium carbonate extender white (Payne, 1961).

Ground white dolomitic limestone or even ground dolomite (CaCO $_3$.MgCO $_3$) may occasionally be encountered in works of art (Kühn, 1969, p. 106). Riederer (1974) identified a special variety of calcium magnesium carbonate pigment called huntite (CaCO $_3$.3MgCO $_3$) on early Egyptian terra cotta bowls. Huntite is so fine grained (about 1μ) that the rhombohedral crystal form can be seen only with the electron microscope.

Chalk

English: chalk German: Kreide (f.) French: craie (f.) Italian: creta (f.) Spanish: greda Russian: MeA

The Italian name, *creta*, comes directly from the Latin and is the name used by both Pliny and Vitruvius. *Creta*, however, probably had a broader meaning to those early writers and covered various white inerts including white clays and the diatomaceous (siliceous) earths. Augusti (1967) gave a complete discussion of the ancient names for this class of whites in his *I Colori Pompeiani*.

In the modern paint trade, refined chalk is called whiting; also English white, Paris white, and gilder's whiting.

Origin and Occurrence of Chalk

Chalk is a soft, porous, and friable rock that often occurs in thick beds in various parts of the world. Most familiar are the chalk cliffs of Dover, England, and the chalk beds of western Europe that were laid down in the Cretaceous age (fig. 1). Much of the modern chalk used in Belgium comes from quarries in the villages of Harmignies and Elouges near the French border; but the best chalk for artists' use is said to be "Champagne chalk" from northern France (Eddy De Witte, private communication). Well-known sources were at Rouen, Troyes, Orléans, and along the Marne. "Rügener Kreide" comes from the island of Rügen in North Germany; there are also good sources on the islands of Usedom and Wolin at the mouth of the Oder. Augusti (1967) found chalk in paint specimens from Pompeii; Joyce Plesters reported it in the grounds of paintings from Spain (Martin, 1970); and Caley (1946) found evidence of it on Greek antiquities. Pliny stated that white "paretonium" was found in Egypt, Cyrene, and Crete.

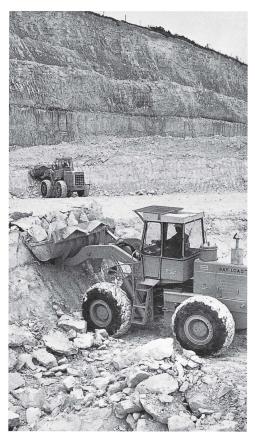


Fig. 1 The working of chalk at the face of a chalk quarry in Wiltshire, England. Courtesy English China Clay Sales Co., Ltd.

"Melinum" came from the isle of Melos and was said to be one of the four colors used by Appelles and other ancient Greek painters (Bailey, 1932). According to Berthelot, Melos earth was known to the Syrian and Arabic alchemists (Loumyer, 1914). Davy (1815) found chalk in the Baths of Titus. Chalk occurs extensively in North America, principally in the southern trans-Mississippi states of Nebraska, Arkansas, and Texas, but it is not as white as the chalk of England and Europe. We know little about its occurrence in Asia and other continents, but it must be present in these locations.

Chalk, which is derived from marine ooze, is largely composed of fossil remains of unicellular algae of the phylum Chrysophyta, class Chrysophyae (golden-brown algae). The principal "nanofossil" remains, which characterize chalk, are tiny disklike forms called coccoliths. These are minute calcareous platelets that in the living orga-

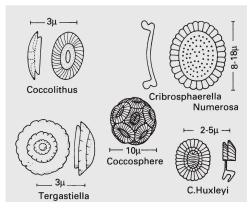


Fig. 2 Coccosphere and various coccoliths (after *McGraw-Hill Encyclopedia of Science and Technology*, vol. 3, p. 249. Copyright 1960 by McGraw-Hill Book Company, Inc. Used with permission of the McGraw-Hill Book Company.).

nism are often bound together to form a spherical shell called a coccosphere (fig. 2). The coccoliths are usually a few (3-8) micrometers in diameter and are oval, discoidal, spherical, or buttonshaped with various perforations and patterns of ornamentation. Coccospheres make up much of the phytoplankton of the northern and southern seas, and are important in the marine food chain. Since coccospheres are plant forms and, hence, need light, they grow most abundantly near the ocean surface. Black (1965), who gave an excellent résumé of this type of microplankton, described how they were first discovered by C. C. Ehrenberg in 1836 and were later described in greater detail by T. H. Huxley and G. C. Wallich. A detailed description with excellent drawings and photomicrographs of various species of Coccolithophoridae is shown in a chapter by Georges Deflandre, "Classe des Coccolithophoridés" in Grassé's (1952) Traité de Zoologie.

Coccoliths are found in calcareous rocks formed in various geological ages from the lower Jurassic to the Recent. The chalk of England and western Europe was laid down in the Upper Cretaceous Period. The Coccolithophoridae have had a long evolutionary history that make them important in dating sedimentary deposits. For more details of coccolith structure and recognition, see Particle Characteristics.

Coccoliths seem to have been first observed by Kozlowski (1950) in works of art; he found them in paintings done on plaster, which he described in the Polish journal Ochrona Zabytków. He also described them in association with a Slavonic limestone figure found in a river bed (Kozlowski, 1965). They were observed soon after by Coremans et al. (1952) on a painting of The Last Supper by the Flemish painter Dieric Bouts. They are shown in high magnification photomicrographs by Augusti in his I Colori Pompeiani, mentioned above. More recently, coccoliths, which could be classified according to their Cretaceous stage, were found in the ground of a Peter Paul Rubens painting, now in the National Gallery of Art, Washington (Feller, 1973). Most surprisingly, coccoliths have been observed by Perch-Nielsen (1973) in the grounds of a number of thirteenth- to fourteenth-century paintings and wood sculptures from Norway. Perch-Nielsen can estimate from the coccolith assemblages whether the chalk came from Belgium, Germany, Denmark, France, or England. There are no chalk deposits in Norway. She said (private communication), "Thus it seems that while chalk was not available in Norway itself, the provenance of the chalk coincides with that of the style for most of the objects investigated in the study."

Preparation of Chalk

In England, the crude quarried chalk is left for a time to weather to aid in the separation of flint nodules that often permeate the chalk beds (fig. 1). The lumps of chalk are then ground under water and the product is washed and allowed to settle in large vats. Toch (1925) reported that the top layer nearest the surface is dried, bulked, and sold as "Paris white," which is the finest and whitest product. The next layers are sold under the name "Extra Gilder's White," and the bottom layer, known as "Commercial White," is used for making glazier's putty. Presumably, chalk was processed in much the same way in medieval times. In the modern paint industry, natural whitings can be further reduced in particle size by a "micronizing" process (Payne, 1961).

History of Use

Natural chalk has a long history in painting going back to classical times (Augusti, 1967). In northern Europe, from early medieval times—particularly in England, France, and the Low Countries—chalk was employed with animal glue for making the ground coat or preparation layer of panel paintings in order to produce a white background and a proper surface for painting. It was

used for painting grounds in much the same way that gesso (gypsum) was used in Italy and Spain. Sometimes lead white (see chapter 3), and later, zinc white were mixed with the chalk to make it denser and whiter. In certain Dutch and Italian canvas paintings of the seventeenth century, chalk has been found as an extender for red and brown ochreous grounds. De Wild (1929) identified "whiting" in thirty-six Early Netherlandish, Dutch, and Flemish paintings ranging in dates from 1430 to 1816. Levigated chalk was used in ancient and medieval times as a mild abrasive for polishing gold and silver.

Chalk was not used alone in oil-medium paints because of its low refractive index and, hence, poor color and hiding power, although this quality has been exploited to achieve translucency in the paint film, for example, in Dutch landscapes (Gifford, 1983). Linseed oil—whiting mixtures have long been used, however, in the preparation of glazier's putty. In modern times it has been used with animal glue or other aqueous media for the manufacture of distemper and calcimine paints for interior walls and ceilings. It is used as an extender pigment to control gloss and texture, to improve consistency and leveling, and to retard pigment settling in paint cans.

Synthetic or Precipitated Calcium Carbonate

Artificial calcium carbonate, formerly called precipitated chalk, is produced as a by-product in a number of modern chemical industries, an example being the recovery of ammonium chloride, which is an intermediate product made in the Solvay process for the manufacture of sodium carbonate from sodium chloride. Precipitated chalk is whiter, more controlled in particle size, and more homogeneous than are natural chalks, and it also differs from natural chalk in that it contains no fossil remains. Besides its use in paints, precipitated chalk is used as a mild abrasive in metal polishes and dentifrices. It is often used as a basis for pastel crayons and also has wide use today in the manufacture of printing inks, plastics, and rubber products. It is especially useful in paper fillers as an alkaline pigment to counteract acidity. P. F. Woerner reported that the manufacture of precipitated calcium carbonate started around 1850 in Birmingham, England, where it was made by treating calcium chloride with sodium carbonate (Patton, 1973). This method was discontinued about 1900 in favor of a direct method where carbon dioxide from the burning of lime is combined with a lime slurry (milk-of-lime) to form the carbonate. There are other methods of manufacture.

Lime White or St. John's White

English: St. John's white Italian: bianco sangiovanni

When limestone or marble or any form of calcium carbonate is strongly heated or calcined at bright red heat (800°-900°C), carbon dioxide is driven off as gas, leaving a white residue of calcium oxide or "quicklime" (CaO). Freshly calcined lime reacts vigorously with water to form calcium hydroxide, Ca(OH)2, simultaneously producing much heat. If just the correct amount of water is added under carefully controlled conditions, the calcium hydroxide is formed as a fine white powder. This is a commercially important product useful in the building trades and chemical industries. If excess water is added, called "water slaking," a paste or putty is produced that-when mixed with sand—forms the mortar used on wall plasters and in bricklaying.

On long exposure to air, the calcium hydroxide combines with atmospheric carbon dioxide to form calcium carbonate; thus, in effect reversing the lime-burning process. This causes the setting and hardening of mortar with age. Quicklime also absorbs water and carbon dioxide from the air, which is called "air slaking."

When water-slaked lime is kept moist in a pit for some weeks, it becomes thick and pasty and different in consistency from freshly slaked lime. This pasty form was used by the Italian painters as a white pigment for fresco painting. Cennino Cennini, in the well-known Il Libro dell' Arte (chapter 58), calls this white bianco sangiovanni (St. John's white after the patron saint of Florence) and tells how it is made by exposing little cakes of lime putty in the air for a long time with occasional regrinding with water and re-forming with more exposure to open air (Thompson, 1933). Cennino emphasized that the white required no binding medium when used for painting frescoes. E. Denninger (private communication) of Stuttgart prepared this white according to the Cennino recipe, and in his description he noted its alkalinity caused by the presence of calcium hydroxide. It is so strongly alkaline that it reacts readily with casein and with eggwhite to form hard insoluble paint films useful for retouching in the restoration of fresco painting. A specimen of lime white (bianco sangiovanni) given to one of the authors

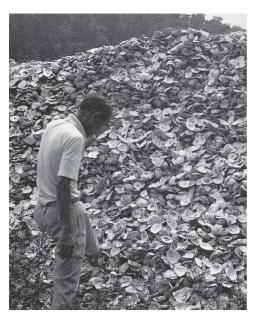


Fig. 3 A mound of oyster shells awaiting processing outside the Nakagawa Gofun Company plant, Uji, Japan, 1970. The man in the picture is Mr. Nakagawa. Courtesy Kazuo Yamasaki, Nagoya, Japan.

(Gettens) by Dr. Denninger in 1964, and since then kept in a stoppered glass vial, still contained calcium hydroxide (portlandite) as shown by x-ray diffraction analysis (see fig. 17).

Shell White

English: shell white Japanese: gofun Chinese: k'o fên

The shells of molluscs are nearly pure calcium carbonate. In sufficient quantities they can be powdered and used for about the same commercial purposes as whiting or ground limestone. The term "shell white" is usually used in European literary sources to describe white made from crushed eggshells. The most often quoted reference is to Lomazzo's "Trattato" of 1584 in which finely ground eggshell (*il guscio delle uoua tridato minutamente*) is recommended as a white pigment for mixing with other colors in fresco painting. Eggshell white and a white made from cuttlefish bone are also mentioned in the Paduan manuscript (c.mid-seventeenth century) transcribed and translated by Mrs. Merrifield.

In Japan, unique use has been made of sea shells, mostly oyster shells, to produce a white pigment for artists called *gofun*, which still enjoys

wide use. In the city of Uji, between Kyoto and Nara, the factory operated by Nakagawa Keiji still [1974] produces gofun by time-honored methods. The small plant on the edge of the city is surrounded by mounds of oyster shells, which are harvested from the Inland Sea. They are left in these mounds to age for a period of up to five years, which permits decomposition and removal of the organic matter in the shells (fig. 3). The preparation of gofun is a fairly simple mechanical process that involves selection, crushing, grinding, and pulverizing in a ball or stamp mill followed by particle-size classification of several steps by water levigation in concrete tanks. Apparently, the shells are not heated or calcined in any part of the process. The finely levigated material is dried out-of-doors in shallow wooden trays. The final product is marketed in the form of chips or dried cake. In Japan, gofun is also used in the manufacture of dolls and other products. It is cheaper to produce than heavy-metal whites and it is not poisonous. Like chalk white, it is not a good white with oil-medium, but despite its low refractive index, it has good hiding power in aqueous medium. It is not a brilliant white like the heavymetal whites, but it has a pleasing eggshell quality so often seen in the flesh tones of Japanese Ukiyo-e paintings (fig. 4). Gofun serves also as a base for tints, especially those made from lowbodied transparent colorants such as indigo or enji. This unique white can be identified microscopically in tiny samples by its fibrous structure (see below). The term gofun means, literally, foreign powder; hence, in the older Japanese literature it may be applied to other whites, including lead white.

Little is known about the earliest use of shell white in Japan. Kazuo Yamasaki (private communication) said that, as far as he knows, the earliest use of gofun on wall paintings in temples is the five-storied pagoda of Hokanji Temple, Yasaka, Kyoto, which was re-erected in the year 1439. He further indicated (Yamasaki & Nishikawa, 1970) that powdered shell replaced clay as a white pigment sometime in the fifteenth and sixteenth centuries. The earliest known occurrence is in the Freer Gallery of Art on a Japanese painting (nos. 71.1 and 71.2), on a pair of six-fold screens by an artist who was active in the early sixteenth century. Shell white seems to have been widely used by Japanese painters since the seventeenth century.



Fig. 4 The white of the flesh tones and crane medallions of the figure is made of pulverized sea shells, probably oyster. The painting, *Courtesan and Two Attendants*, of which this is a detail, was painted on paper by Ishikawa Toyonubu (1711–1785). Freer Gallery of Art, No. 04.195.

Coral

English: coral
German: Koralle (f.)
French: corail (m.)
Italian: corallo
Spanish: coral
Russian: κοραλλ
Japanese: sango matsu

Ground coral, which is usually warm pink in tone, is included here because it also is essentially calcium carbonate. The white form of coral used to be cheaper and quite common in Europe, for example, in Italy. It probably came from the North African coast. There do not seem to be any references in European literary sources to the use of crushed coral as a pigment, however. Ground coral is sold by Japanese art supply dealers who call it *sango matsu* (coral powder). Apparently, it is a specialty pigment employed for decorative effects, like ground rock crystal, agate, and mica.

The reef-building algae and corals are com-

posed of both calcite and aragonite (Goreau, 1963). A sample of a coarse pink powder labeled sango supplied by Ishida Hōkōdō Company of Kyoto gives an x-ray powder pattern of calcite. The coarse particles are even in size (probably classified by levigation) and show laminar structure. Microscopically the particles are nearly colorlèss and translucent (see fig. 15).

Color

The powdered forms of all varieties of calcium carbonate, if moderately pure, are white, but do not possess the high scattering or hiding power in drying oil-base paints as do the heavy-metal whites. Natural chalk is usually a grayish white or yellowish white rock, depending on the amount of impurities present, especially iron oxide. Commercial whiting is prepared from the whitest deposits, situated largely in England and western Europe. White paint made from whiting and glue medium or from shell white has a translucent matte quality pleasing in appearance. Precipitated chalk, capable of high purity and fine particle size, provides the whitest and brightest of the calcium carbonate pigments.

Calcium carbonate reflects and transmits light fairly constantly in both the visible and ultraviolet as far down as 297 nm, falling off slightly at the low wavelengths (Pfund, 1923; Stutz, 1926).

Optical Properties of Calcite

Calcite belongs to the hexagonal-rhombohedral system and has perfect cleavage parallel to the unit rhombohedron {1011} (fig. 5). In nature it crystallizes in a variety of habits. In finely divided samples, rhombohedral cleavage fragments are parallel to the major diagonal (fig. 6), although they can be seen oblique to the long diagonal in some sections. Calcite has two principal refractive indices according to the orientation of the crystal as light passes through it: $\varepsilon = 1.486$, $\omega = 1.658$, uniaxial negative. The birefringence is high, 0.172, but it is lower than that of ankerite, magnesite, and siderite, and some other natural carbonates (see fig. 7). In the usual rhombs it is not possible to observe ε , but only a higher value of ε' , which is about 1.566 for pure calcite.

Because of its high birefringence, calcite "twinkles" as the microscope stage is rotated. High relief appears when the long diagonal (and the usual twin planes) is in the vibration plane of the polarizer (usually N–S or vertical) and low relief is observed when the short diagonal is in this direction.

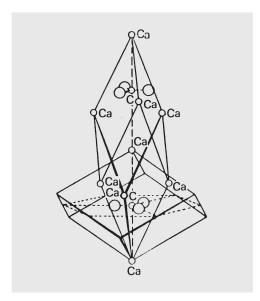


Fig. 5 The structure of calcite. The elongated cell is the true rhombohedral unit cell (Z=2); the cleavage rhombohedron cell corresponding to a face-centered rhombohedron is also shown. (After P. P. Ewald and C. Hermann, 1931, *Strukturbericht* 1913–1928 [Ergänzungsband der *Zeit. Krist.*] Leipzig.)

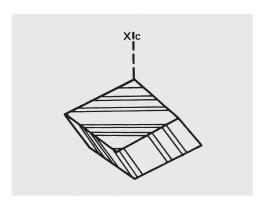


Fig. 6 Cleavage rhomb of calcite showing position of characteristic twinning planes parallel to the long axis. The dotted line shows the position of the optic axis and the *c* crystallographic axis. (After W. E. Tröger, *Optische Bestimmung der Gesteinbildenden Minerale*, Stuttgart 1971, p. 33.)

Extinction is symmetrical with the cleavage faces in calcite, dolomite, and ankerite.

If the microscope is defocused upward, a uniaxial figure can be observed with an eccentric figure if the stage is rotated. This can be observed even

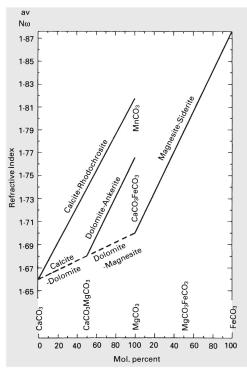


Fig. 7 Variations of N_{ω} with composition in the rhombohedral carbonates. (After George C. Kennedy, "Chart for Correlation of Optical Properties with Chemical Composition of Some Common Rockforming Minerals," *American Mineralogist* 32 [1947], 561–573.)

on tiny fragments of chalk that turn distinctly yellow and blue when a gypsum retardation plate is used—those that blink distinctly under crossed polars when the stage is rotated. In *gofun*, most of the smaller fragments show inclined extinction at variable angles and appear to have negative elongation. Aragonite is orthorhombic; $\alpha = 1.530$, $\beta = 1.683$, $\gamma = 1.686$, biaxial negative. For further description, see *The Particle Atlas* (McCrone et al., 1967, p. 150).

Physical Properties

Specific gravity of calcite is 2.714; other forms range from 2.68–2.72. Hardness is about 3, but varies with the direction of the cleavage face. Aragonite has a specific gravity of 2.95 and a hardness of 3.5–4. Aragonite, the principal polymorph of calcite, is relatively unstable in respect to calcite and consequently is less abundant in nature. Dana indicated that it is often converted to

calcite accompanying changes of environment. Some sea shells are composed entirely of aragonite; other shells are a mixture of aragonite and calcite and some are completely calcite (Galtsoff, 1964).

Chemical Properties

Calcite is stable under ordinary circumstances, which is one reason why it is so abundant in nature. As mentioned earlier, when heated above red heat, all forms decompose with formation of calcium oxide (CaO) and evolution of carbon dioxide gas. It is decomposed readily by mineral acids with rapid evolution (effervescence) of carbon dioxide gas. The finer the calcite form, the more rapid the decomposition. Simultaneously, corresponding calcium salts are formed; calcium nitrate with nitric acid and calcium chloride with hydrochloric acid. Both these salts are deliquescent, and so do not crystallize well from aqueous solution. Calcium sulfate formed with sulfuric acid however crystallizes well in needlelike crystals, which serves as a microchemical test for calcium (see fig. 16).

All forms of calcium carbonate are alkaline, ranging from a pH of 7.5 for ground limestone to 9.8 for precipitated chalk (Lukens, 1941).

Permanence and Compatibility

All varieties of calcium carbonate are permanent when exposed to light. They are not darkened by hydrogen sulfide gas or by contact with sulfide pigments. They are compatible with most other pigments except the alkali-sensitive colors such as Prussian blue; this pigment may be discolored by lime white, which can retain its alkalinity for some time. The acids in modern industrial and urban atmospheres, however, are destructive, especially to the more finely crystalline and porous varieties of calcite. Calcium sulfate, which is formed in the presence of sulfuric acid, has greater volume than the carbonate, causing spalling and flaking of lime surfaces. This reaction has caused much mischief to frescoes in Italy and to limestone and marble buildings all over Europe (Sayre & Majewski, 1963). As a component of the grounds of European panel paintings, chalk seems little affected because it is protected by the glue binder and overlayers of paint. Shell white in Japanese paintings, however, would be subject to attack if exposed to polluted industrial and urban atmospheres.

Purity of Composition

Chalk is a fairly pure carbonate of lime, many specimens analyzing as 94%–98% CaCO₃, with minor impurities of MgCO₃, SiO₂, and (FeAl)₂O₃ (Pirsson, 1908). Where local materials were used in painting, specific impurities at rather greater concentrations may be present in the source of calcium carbonate. For example, the ground layer of the Herlin altarpiece at Bopjingen, southern Germany, was found to comprise a mixture of calcium and magnesium carbonates, the latter probably in the form of dolomite (Rieber & Straub, 1977).

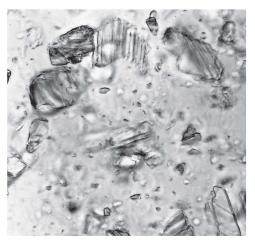


Fig. 8 Finely ground particles of Italian marble (marble dust) are fractured in appearance and irregular in size and shape. The striae caused by twinning planes are visible.

A. By transmitted light (mounted in Canada balsam n = 1.55) at 500x.



B. Same specimen in crossed polars. Sample courtesy English China Clay Sales Co., Ltd., St. Austell, Cornwall, England.

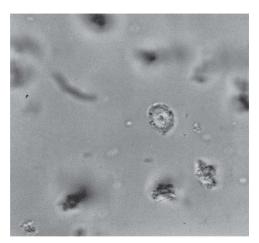
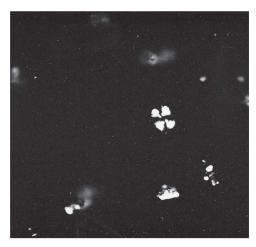


Fig. 9 A. The single oval-shaped coccolith shown is from the chalk ground of a panel painting, *The Annunciation*, by the Master of Liesborn, National Gallery, London, No. 256.



B. The same particle, when viewed between crossed polars, shows a black cross which results when birefringent platelets within the coccolith are aligned in the polarizing planes. 1,000x magnification, mounted in Aroclor (n = 1.66). Specimen courtesy of Joyce Plesters.

Calcium carbonate content of commercial natural whitings ranges from 95% to 99.5% (Scofield & Edwards, 1974). CaCO₃ content of precipitated chalks averages better than 99%. A spectrographic analysis of calcined oyster shell from Japan, prepared at the Freer Gallery of Art, showed total impurities of less than 1%, half of that being magnesium. Kazuo Yamasaki (private communication), however, reported a wet chemical analysis of a sample of "gofun" commercially obtained as fol-

lows: CaCO₃ 94.99%, (FeAl)₂O₃ 0.70%, insoluble matter 1.83%; total 97.52%.

Identification

Calcium carbonate, as such, is one of the easiest materials to identify by chemical and microscopical methods. It is more difficult to identify the specific varieties as recognition is largely dependent on study of the particle characteristics under the microscope.

Particle Characteristics

Calcite. Very little of pure powdered rock calcite is found in art objects. The nearest to it is powdered marble or marble dust and perhaps occasionally powdered limestone. Marble consists of the compact interlocking grains of calcite, which are transparent when pure. The fragmented grains in marble dust show all the characteristics of calcite. Cleavage planes and twinning of calcite crystals may be visible (fig. 8). For a more complete description, see *The Particle Atlas* (McCrone et al., 1967, p. 153).

Chalk is finely particulate and, as mentioned in its general description, is characterized by the presence of coccoliths, which are usually tiny round or oval forms and quite difficult to see microscopically in ordinary transmitted light even at high magnifications. They are best seen under crossed polars at magnifications of 500x and above. If properly oriented, many coccoliths show a curved black cross, something like a fat pinwheel in ap-

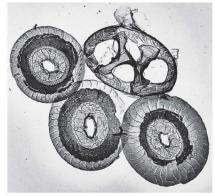


Fig. 10 Coccoliths from North Atlantic deep-sea deposits of the Eocene Age. The larger coccolith with cross members is *Neococcolithes dubius* (Deflandre) Black. The others are genus *Ericsonia* sp. Platinum—carbon replica by transmission electron microscopy, enlarged to c. 3,360x. Courtesy of Kenneth Towe, Smithsonian Institution.

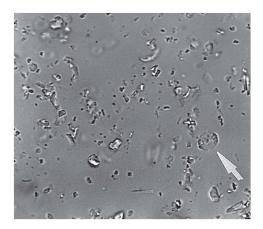
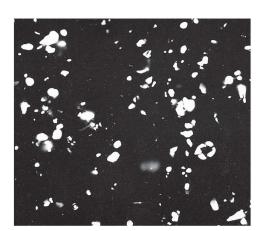


Fig. 11 Commercial whiting made from natural chalk contains scattered fossil oval and rounded forms called coccoliths (arrow).

A. In transmitted light they are difficult to see, even at this magnification of 1,000x (oil-immersion lens).

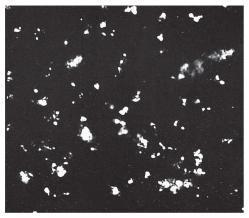


B. In crossed polars they show a characteristic black cross (see also fig. 9). The specimen was mounted in Aroclor (n = 1.66). Sample from Hopkins, Parris and Sons, London. Specimen courtesy of Joyce Plesters.



Fig. 12 Precipitated chalk is made chemically. The particles are fine and fairly uniform in size, but without characteristic shape.

A. Taken in transmitted light at 1,000x with oil-immersion lens; the specimen was mounted in immersion liquid (n = 1.80).



B. Same specimen in crossed polars. Whittaker 2923, USP Domestic.

pearance. These dark crosses result when birefringent platelets within the coccolith are aligned in the polarizing planes of the polars, usually in N–S and E–W directions (figs. 9 and 11); some fine examples are shown by one of the authors (Feller, 1973).

Coccoliths are often accompanied by tiny rodlike fragments called rhabdoliths. Both are so small that structural details are best seen in electron micrographs (figs. 10 and 19B). The majority of the particles in chalk are simply broken coccolith fragments without recognizable form.

Precipitated chalk is finely particulate and uniform in size; each particle is a single, whole, strongly birefracting crystal, but without recognizable shape since they are formed rapidly in a chemical precipitate. There are no coccoliths or other organic forms, although there may be scattered rosettes which might be mistaken for them (fig. 12). Particle characteristics might be affected by the method of manufacture. For a more detailed description, see *The Particle Atlas* (McCrone et al., 1967, p. 256). Butcher (1934) also shows photomicrographs of precipitated chalk.

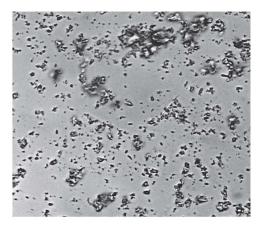
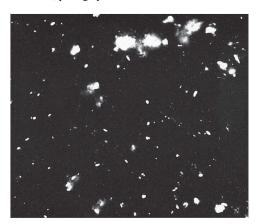


Fig. 13 The particles of lime white (bianco sangiovanni) are very fine and without characteristic shape even at magnification of 1,000x seen here. A. By transmitted light mounted in immersion liquid, n = 1.80, photographed with oil-immersion lens.



Fig. 14 *Gofun* (shell white) from Japanese painting. Freer Gallery of Art, No. 98.95. A characteristic feature is the predominance of lath-shaped particles. Crossed polars, 385x. In Canada balsam (n = 1.55).



B. Same field in crossed polars. Sample courtesy E. Denninger, Stuttgart.

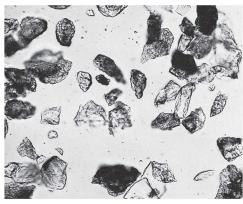
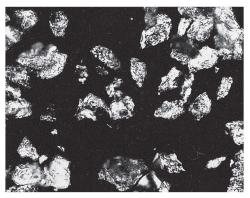


Fig. 15 Coral (sango matsu), coarsely ground. Japanese pigment purchased in Japan in 1956 by Doanda Wheeler Randall. 150x.

A. In transmitted light.

Lime white in the single specimen available is very uniform and finely particulate, finer than precipitated chalk (fig. 13).

Shell white (gofun), although finely particulate, is not uniform in particle size or shape. The particles are elongated, flat, and lathlike in shape and somewhat fibrous, and in this way they reflect the mode of deposition of calcite at the edge of the growing mollusc shell (Wilbur & Yonge, 1964). The particles are usually so thin that only first-order gray interference colors are seen in polarized light (fig. 14).



B. Same field in crossed polars. Mounted in Canada balsam (n = 1.55).



Fig. 16 Microchemical test for calcium. When calcium carbonate is dissolved in dilute hydrochloric acid and then a drop of dilute sulfuric acid is added, needlelike crystals of CaSO₄.2H₂O (gypsum) form at the edge of the test drop. Photomicrograph, 89x, transmitted light without cover glass.

Observation of particle characteristics of pigments by transmitted light microscopy has certain advantages, especially in that it permits recognition of color and internal structure. Scanning electron microscopy on the other hand, as shown in figure 19, permits study of outward particle characteristics at a higher order of magnification and with greater depth of field. Here, it shows significant differences among calcium carbonate whites from different sources. These micrographs were made, however, from reference samples of known origin and purity. It is quite another matter to get good scanning electron micrographs of specimens from paintings, since here the presence of media and impurities may interfere, although an enzymatic method of removing the glue medium from samples of chalk grounds has proven successful (Winter, 1975). Scanning electron microscopy of paint specimens still offers a real challenge.

Microchemical Tests

It has been mentioned previously that calcite in its various forms is one of the most easily identified substances. Presence of the carbonate radical is indicated by strong evolution of gas bubbles (effervescence) even when the tiniest particle is touched with a drop of dilute hydrochloric acid on a microscope slide. It is ordinarily unnecessary to test for carbon dioxide because there are few substances other than carbonates that evolve a gas so readily, but a test can be made for carbon dioxide even on a microscale. Ca2+ can be identified by using dilute sulfuric acid in place of hydrochloric acid. Directly after addition of the acid to a particle of the white pigment, small clusters or rosettes of needlelike crystals of calcium sulfate dihydrate (CaSO₄.2H₂O) form. A better method is first to dissolve the white particle in dilute hydrochloric acid, observe the evolution of gas, and then add to the first drop a second drop of dilute sulfuric acid. The same crystals of calcium sulfate dihydrate form but more slowly and in more perfect needlelike shape. A paint particle half the size of a dot on this page suffices for each test (fig. 16).

Feigl (1972) gave a sensitive spot test for soluble calcium salts with aqueous 0.2% sodium rhodizonate in the presence of 0.5M NaOH, which may be applied to specimens of calcium carbonate once brought into solution. A violet precipitate is formed.

Criteria for Positive Identification

X-ray diffraction analysis is the most positive means of identification of calcium carbonate. However, calcium carbonate can also be identified through the following observations: extraordinarily high birefringence, as observed under crossed polars, combined with low refractive index (as opposed to heavy-metal whites); rapid decomposition of the material in dilute acid; and a microchemical test for Ca2+ with dilute sulfuric acid. Identification of the specific type of calcium carbonate requires microscopic examination of carefully mounted samples by transmitted light, followed, if possible, by microscopic comparison of the unknown with known specimens. Scanning electron microscopy might prove useful in distinguishing varieties.

Emission Spectrographic Analysis

The prominent lines for calcium in the D.C. arc are 4454.8, 4226.7, 3968.5, 3933.7, 3179.3, and 3158.9 Å. The standard sensitivity for calcium is 0.001% (Waring & Annell, 1953).

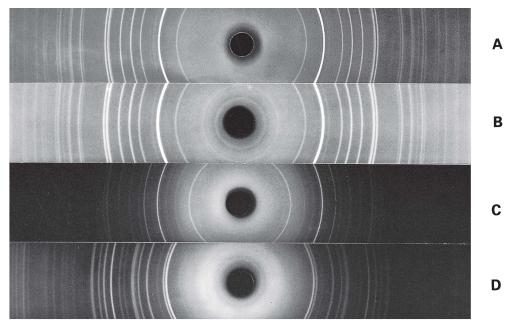


Fig. 17 X-ray diffraction patterns for calcium carbonate whites.

A. Calcite. Marble 300. Italian marble dust. English China Clay Sales Co., Ltd., St. Austell, Cornwall, 1973.

B. Gofun (shell white). Japanese commercial dry pigment.

X-ray Diffraction

Since calcium carbonate has a well-ordered molecular structure, it gives a strong and sharp x-ray diffraction pattern: the d spacings and intensities of calcite and aragonite are given in table 1. Some typical powder patterns are shown in figure 17.

A method for quantitatively analyzing the calcite–aragonite ratio in precipitated chalk was reported by Cox and Goodwin (1933). This ratio can be estimated by infrared spectroscopy as well (see below).

X-ray Spectrometric (X-ray Fluorescence) and Electron-Probe Microanalysis

The $K\alpha_2$ line of calcium at 3.69 keV is the most sensitive line in x-ray fluorescence analyses, although the $K\beta_1$ at 4.01 keV is also detected using ⁵⁵Fe or ¹⁰⁹Cd sources (Hansen, 1973).

Infrared Absorption Spectroscopy

The calcite, magnesite, smithsonite, dolomite, rhodochrosite family of carbonate minerals and

C. Lime white (St. John's White; bianco sangiovanni), prepared by E. Denninger, 1964. Mixture of calcium carbonate and calcium hydroxide (marked).

D. Aragonite mineral. Austria. Department of Mineral Sciences, Smithsonian Institution, specimen R2519. Photographs not to be used for measurement purposes. XRD patterns by Elisabeth West FitzHugh.

the aragonite, strontianite, cerussite, and witherite family may be identified by means of their infrared absorption bands. Quantitative applications allow determination of calcite-dolomite ratios in minerals and calcite-aragonite ratios in shell material. Table 2 lists the wavelengths of the key absorption bands of the minerals, and table 3 shows the fundamental absorptions of the carbonate ion in the infrared and Raman for calcite and aragonite (Nakamoto, 1978). The spectra in the far infrared have been reported by Angino (1967). Analyses of this type may be carried out on a milligram or less of material. A common method is to grind the sample in potassium bromide crystals and to compress the mixture into a translucent pellet which, in turn, is mounted in the spectrometer (Huang & Kerr, 1960). Riederer (1974) confirmed the presence of the calcium magnesium carbonate mineral pigment called huntite by this method.

Low and Tascon (1985) also recorded the infrared spectra of calcite and aragonite using the new technique of photothermal beam deflection spectroscopy.

Table 1 X-ray Diffraction Data for Calcium Carbonate

Calcitea

Cu: 1.5405 Å, 26°C					Arago Cu: 1.505	лие- 5 Å, 26°С	
d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
3.86 (3.852)	12 (29)	1.297	2	4.212	2	1.698	3
3.035 (3.030)	100 (100)	1.284	1	3.396	100	1.557	4
2.845 (2.834)	3 (2)	1.247	1	3.273	52	1.535	2
2.495 (2.495)	14 (7)	1.235	2	2.871	4	1.499	4
2.285 (2.284)	18 (18)	1.1795 (1.1779)	3 (3)	2.730	9	1.475	3
2.095 (2.094)	18 (27)	1.1538 (1.1536)	3 (3)	2.700	46	1.466	5
1.927 (1.926)	5 (4)	1.1425 (1.1417)	1 (3)	2.481	33	1.411	5
1.913 (1.907)	17 (17)	1.1244	1	2.409	14	1.404	3
1.875 (1.873)	17 (34)	1.0613	1	2.372	38	1.365	3
1.626 (1.626)	4 (2)	1.0473 (1.0471)	3 (2)	2.341	31	1.358	3
1.604 (1.604)	8 (15)	1.0447 (1.0440)	4 (2)	2.328	6	1.328	2
1.587 (1.582)	2 (2)	1.0352	2	2.188	11	1.261	6
1.525 (1.525)	5 (3)	1.0234	1	2.106	23	1.240	7
1.518	4	1.0118	2	1.977	65	1.224	5
1.510 (1.506)	3 (2)	0.9895	1	1.882	32	1.205	6
1.473	2	0.9846	1	1.877	25	1.1892	5
1.440 (1.441)	5 (5)	0.9782	1	1.814	23	1.1712	6
1.422 (1.417)	3 (3)	0.9767	3	1.759	4	1.1599	3
1.356	1	0.9655	2	1.742	25		
1.339 (1.336)	2 (3)			1.728	15		

a. JCPDS File No. 5-586 (measured pattern) in brackets, JCPDS File No. 24-27 (calculated pattern).

Neutron Activation Analysis

There are three radioactive isotopes of calcium that may be produced by neutron activation which, under certain conditions, may lead to useful analyses for calcium. The short-lived isotope, ⁴⁹Ca (half-life approximately nine minutes), is useful for the rapid, sensitive analysis of trace amounts of calcium if the analysis can be carried out in the proximity of a nuclear reactor. Another isotope, ⁴⁷Ca, with a longer half-life (approximately five days), is the activation product of ⁴⁶Ca, which, unfortunately, has an extremely low abundance. Hence, it is useful only when calcium is present as a major constituent.

The above isotopes can be detected without the use of post-irradiation chemical separations because their gamma-ray emissions can be measured using a lithium-drifted germanium detector and pulse-height spectroscopy. An isotope with a half-life of approximately 160 days, ⁴⁵Ca is the activation product of ⁴⁴Ca, which has a reasonable abundance and can lead to a fairly sensitive analysis. However, as a pure beta-ray emitter, it is useful

only if a chemical separation is performed following activation (Bernard Keisch, private communication).

Aragoniteb

X-radiography

Since calcium carbonate is a low-density pigment, it is quite transparent to x-rays (see fig. 18). De Wild (1929) gave the mass absorption coefficient of CaCO₃ as 8.6 for a wavelength of 0.709 Å.

Occurrences of Chalk (CaCO₃) in Paintings of European Schools

Examined in the Scientific Department of the National Gallery, London

(Reported by Joyce Plesters, private communica-

Most of the occurrences listed are from pictures in the National Gallery's own collection; the remainder are from paintings or works of art of which the provenance, attribution, and dating are generally accepted.

With two exceptions, the chalk was always

b. JCPDS File No. 5-453.

⁽Courtesy of JCPDS International Centre for Diffraction Data, 1983.)

Table 2 Infrared Absorption Wavelengths for Carbonate Identification Peaks (after Chester and Elderfield, 1967)

Identification Bands

Wavelengths in µ				Wave N	umbers i	n cm ⁻¹
Magnesite		11.30	13.40		885	747
Dolomite		11.38	13.76		879	727
Calcite		11.41	14.08a	_	877	711
Aragonite	9.23	11.67	14.08a	1084	857	711ª
Strontianite	9.35	11.67	14.34a	1070	857	698
Witherite	9.43	11.67	14.56	1061	857	687
Cerussite	9.52	11.91	14.78	1051	840	677

a. The minerals can be distinguished because aragonite has a double peak.

Table 3 Fundamental Vibrations of the Carbonate Ion in Calcite and Aragonite. Absorption Bands in Wave Numbers (cm⁻¹)

		ν ₁ Symmetric Stretch	$ u_2 \\ Out of Plane \\ Bend $	$ u_3 $ Asymmetric Stretch	ν ₄ Asymmetric Stretch
Calcite	IR	inactive	879	1429–1492	706
	Raman	1087	inactive	1432	714
Aragonite	IR	1080	866	1504, 1492	711, 706
	Raman	1084	852	1460	704

present as the white inert of the ground, invariably bound with animal glue. In the majority of occurrences listed, chalk was the only component of the ground besides animal glue (disregarding small amounts of impurities, such as iron oxide). A few seventeenth-century Italian and Dutch instances have been noted in which calcium carbonate has been detected in a ground layer by x-ray diffraction in mixture with ochre pigments. Most of the occurrences recorded are of white or whitish chalk grounds on wood panel supports and from northern European schools of painting.

Identification was, for the most part, carried out by a combination of microscopic examination and chemical microscopy; but, where mixtures of white inerts or pigments were suspected, an x-ray diffraction powder pattern of the sample was made. Some of the pure chalk specimens have also been confirmed by x-ray diffraction. Often, the examination of the ground of the painting was only incidental to that of the paint layers or pigment so that only occasionally has a sample of ground identified chemically as calcium carbonate been confirmed by further examination to be nat-

ural chalk. When this was done, inspection of the sample, crushed and suitably mounted for study by transmitted light, usually revealed at a magnification of c.250–500x fragments of microfossils (usually of ringlike form), and occasionally calcite particles and quartz fragments.

British School

The inert of the white ground is chalk in the following: *Retable of Five Scenes from the Passion* (oak panels), Norwich School, end of the fourteenth century, Norwich Cathedral (see also Plummer, 1959); six English School portraits (oak panel), sixteenth century; a series of wall decorations on panel, Chichester Cathedral, dated c.1530–1535; a series of early seventeenth-century Scottish ceiling paintings (glue distemper on wood panel), including those at Crathes Castle, Prestongrange House, Rossend Castle, Somerville House.

Calcium carbonate combined with lead white has been found in the grounds of pictures by William Hogarth (nos. 113–118), and a portrait by Thomas Gainsborough (no. 684).



Fig. 18 A. Detail from D. Bouts' *The Entombment*, glue tempera on canvas, c.1455. National Gallery, London, No. 664. Reproduced by permission of the Trustees.

B. X-radiograph detail of the Virgin's head in the Bouts. The upper part of the cowl is painted in chalk as the white pigment, and consequently is rather transparent to x-rays. The flesh paints also contain chalk as a pigment, highlighted with small quantities of lead white.



Early Netherlandish School

The inert of the white ground is chalk in twentynine paintings, all on oak panel supports, including works of Rogier van der Weyden, Dieric Bouts, Hans Memling, Jan Gossaert, Gerard David, Quentin Massys, and Lucas van Leyden, in the National Gallery, London, collection. In a single example, a *Tüchlein* in glue tempera medium by Dieric Bouts, *The Entombment* (no. 664), chalk was found to have been used as the principal white pigment for the flesh tones, with the highlights alone executed in lead white (see fig. 18) (Bomford & Roy, 1986).

German School

The inert of the white ground is chalk in nineteen paintings on wood panels, dating from c.1450–1550 and including works of Hans Holbein the Younger, Hans Baldung (Grien), Stefan Lochner, Albrecht Dürer, Albrecht Altdorfer, the Master of St. Bartholomew, the Master of Liesborn, and the Master of Cappenberg in the National Gallery collection. One other picture, National Gallery, no. 6320, Altdorfer's *Landscape with a Footbridge*, is on vellum stuck down on wood panel, and there is a thin chalk ground on the surface of the vellum.

Flemish School, c.1600

Many of the paintings in this group, whether on canvas or wood panel, do not have chalk grounds. However, a special study of the grounds of pictures by Peter Paul Rubens (Plesters, 1970) revealed that twelve panel paintings had chalk grounds while several others had white grounds consisting of a mixture of calcium carbonate and sulfate in varying proportions.

Dutch School, c.1600

Again, many of the paintings of this school, whether on canvas or wood panel, do not have chalk grounds. However, a study of grounds of paintings by Rembrandt in the collection of the National Gallery, London, revealed that all six painted on wood panel had chalk grounds.

The two paintings by Jan Vermeer in the National Gallery, London, no. 1383, A Young Woman Standing at a Virginal, and no. 2568, A Young Woman Seated at a Virginal, both have light gray grounds consisting of a mixture of chalk with lead white (colored with traces of ochre pigments and carbon black) in oil-medium (see also Kühn, 1968).

French School

Only one panel painting of this school has had its ground specifically examined in the National Gallery Scientific Department, London, up to the present time: Charlemagne, and the Meeting of Saints Joachim and Anne at the Golden Gate (no. 4092), attributed to the studio of the Master of Moulins, has a natural chalk ground on an oak panel. However, an interesting occurrence of chalk, as the white pigment, used either alone or to lighten other pigments, is in the pastel portrait by Jean-Baptiste Perroneau, A Girl with a Kitten (no. 3588, signed and dated 1745, and executed on paper). Gypsum is more commonly recommended and found as the white pigment in pastels.

Italian School

This comes under "Notable Omissions" rather than "Notable Occurrences." Although Italian School paintings probably account for more than half of all the pictures so far examined in the National Gallery Scientific Department, a chalk ground has never so far been identified in a single one, the grounds being invariably of gesso (calcium sulfate in varying proportions of anhydrite and hydrated forms).

It might be noted, however, that occasionally when the white or cream-colored gesso grounds of Italian paintings are treated with dilute acids, slight effervescence of CO, occurs, indicating the presence of carbonate, although no cations other than calcium are found to be present, and recrystallization from dilute acid gives a high yield of gypsum crystals from the sample. A further observation was made in the case of Donatello's Repentant Magdalen, a polychrome statue from the Baptistry, Florence, the gesso of which was found to contain an appreciable proportion of calcium carbonate. The x-ray diffraction powder pattern, kindly carried out for us by R. J. Davis of the British Museum (Natural History), showed a mixture of anhydrite (anhydrous calcium sulfate) and calcite. Dr. Davis initially suggested the possibility that, during the burning of the raw gypsum to make gesso, overheating might have occurred, perhaps in small local spots, to produce calcium oxide, which subsequently may have taken up water and carbon dioxide to convert to calcium carbonate. Dr. Davis later, however, was inclined to abandon this hypothesis in favor of calcite being an impurity in the original mineral gypsum. On the other hand, the analyses of calcium sulfate grounds in Italian paintings made by Gettens and Mrose (1954) and by Bones (1954) gave no indication of calcium carbonate as an impurity in raw gypsum or in gesso grounds, so that further investigation of the subject is probably indicated.

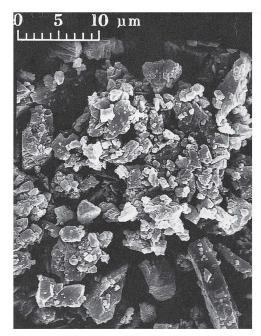
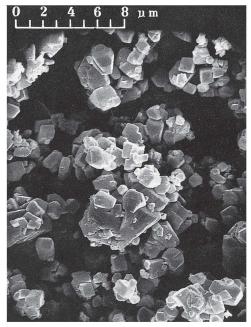
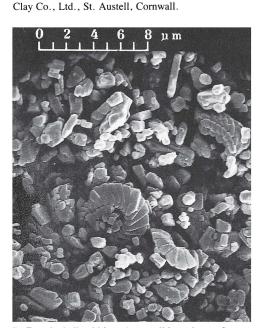


Fig. 19 Scanning electron micrographs of various calcium carbonate white pigments. A. Italian marble dust. The fractured surfaces, irregular shapes, and uneven particle size are plainly

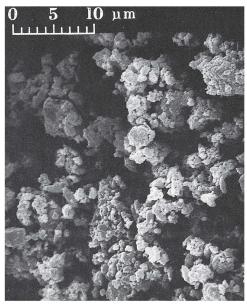
evident. 959x. Sample courtesy of English China



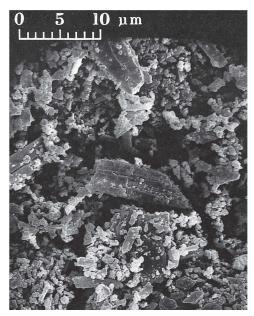
C. Precipitated chalk. The crystal habit of individual particles is apparent. The particle size is small and fairly even, which is characteristic of rapidly formed crystals. 1,598x. Sample from Whittaker 2923.



B. French chalk whiting. A coccolith made up of overlapping calcite platelets shows in the center. The fairly even-sized, rounded particles are mostly coccolith fragments. 1,598x. Sample from Pleuss-Stauffer, 1966.



D. Lime white. The particle shape is irregular and the particle size is the finest of any of the samples shown here. 959x. Sample prepared by E. Denninger.



E. Oyster shell white (gofun). The particle shape is irregular and some fractured surfaces are evident. A structure can be seen in some of the larger particles. 959x. Freer Gallery of Art pigment collection, Furuzawa 31.

All photographs in fig. 19 courtesy of John Winter, Freer Gallery of Art and Walter R. Brown, National Museum of Natural History, Smithsonian Institution.

Notable Occurrences

Chalk on Western Paintings or Painted Objects

Date	Artist/Country, Title, Description, Collection or Location	Analyst and Method of Identification
10th-16th C	European 19 illuminated manuscripts, Paris, Bibliothèque Nationale and Archives Nationales	F. Flieder (1968), micr. (ident. as calcite) (p)
13th-14th C	Norway 27 medieval paintings and sculptures	K. Perch-Nielsen (private communication) (g)
2nd half 13th C	Norway Virgin and Child polychrome wood sculpture, University Museum of National Antiquities, Oslo	U. Plahter and S. Wiik (1970) micr. (g)
2nd half 13th C	Norway 3 altar frontals Church of Tingelstad	K. Perch-Nielsen (Plahter & Plahter, 1972), micr. (g)

⁽p) The calcium carbonate occurs in the paint film proper. In other instances mentioned in these tables, the calcium carbonate has been identified in the ground or preparation of the object concerned (g).

Date	Artist/Country, Title, Description, Collection or Location	Analyst and Method of Identification
early 14th C	English Coronation Chair, Westminster Abbey	S. Rees Jones (1954) micr. (g)
15th–19th C	Dutch and Flemish 36 paintings	A. M. de Wild (1929), micr. (g)
1466	German Herlin altarpiece, polychrome sculpture, Church of St. James, Rothenburg	M. Broekman-Bokstijn et al., (1970) micr., infrared spec. (g)
early 16th C	Antwerp School Panel painting Fogg Art Museum	E. W. FitzHugh, micr. (p)
17th C	Jan Vermeer 35 paintings Private and public collections	H. Kühn (1968) micr., emission spec., x-ray diffraction, infrared spec. (g)
17th–18th C	Austrian 19 sculptures Churches in upper-Austria	F. Mairinger and G. Kerber (1970) x-ray diffraction, micr. (calcite and dolomite [g])
1612–1614	Peter Paul Rubens Descent from the Cross Antwerp Cathedral	P. Coremans and J. Thissen (1962) micr. (g)
c.1630	Peter Paul Rubens Gerbier Family, no. 2558 National Gallery of Art, Washington	R. L. Feller (1973) (p and g)
n.d.	Flemish St. Luke Making a Portrait of the Virgin Fogg Art Museum, no. 106	R. J. Gettens (Stout, 1933) micr. (g)
n.d.	German 76 paintings Schack-Galerie, Munich	H. Kühn (1969) micr., x-ray diffraction, emission spec. (g)
early 19th C	Joseph Mallord William Turner Colletion of painting materials Tate Gallery, London	N. W. Hanson (1954) emission spec.
Calcium Carbona and Sculpture ^a	ate Pigments in the Grounds of Some Dut	tch and Other European Paintings

1466	Friedrich Herlin	L. Vos (g)
	Herlin Altar (polychromed sculpture)	microchemical analysis
	Church of St. James, Rothenburg,	
	West Germany	
1471–1481	Michael Pacher Altarpiece, sculpture and panels	P. Hallebeek (g) x-ray diffraction ^b
	Pfarrkirche, St. Wolfgang, Austria	

^a Reported by P. B. Hallebeek of the Central Research Laboratory for Objects of Art and Science, Amsterdam.

^b Mixture of calcite and dolomite.

⁽p) The calcium carbonate occurs in the paint film proper. In other instances mentioned in these tables, the calcium carbonate has been identified in the ground or preparation of the object concerned (g).

Date	Artist/Country, Title, Description, Collection or Location	Analyst and Method of Identification
1504	The Master of Alkmaar Seven Mercies Rijksmuseum, Amsterdam	C. M. Groen (g) microchemical analysis
1526	Lucas van Leyden Last Judgment Museum "De Lakenhal," Leyden, The Netherlands	P. Hallebeek (g) x-ray diffraction
c.1530	Jan van Scorel Triptych, Aartsbisschoppelijk Museum, Utrecht, The Netherlands	L. Vos (g) microchemical analysis
1764	Thomas Bardwell Portrait of Maurice Suckling National Portrait Gallery, London	P. Hallebeek (g) x-ray diffraction
Calcium Carbon	ate Pigments on Near Eastern and India	n Objects
Middle Kingdom	Egyptian Bersheh sarcophagus Museum of Fine Arts, Boston	R. E. Ogilvie (1967) electron beam microprobe (g)
3rd C A.D., Roman	Egyptian Fayum portrait Toledo Museum of Art, Toledo	R. L. Feller (Buck & Feller, 1972) (g)
14th C	Byzantine Wall paintings Church of Sancta Sophia, Trebizond	J. Plesters (1963) micr. (p)
early 14th C	Byzantine Wall painting Church of the Kariye Çamii, Istanbul	R. J. Gettens (Gettens & Stout, 1958) micr. (p)
late 15th or early 16th C(2); 18th C(1)	Nepalo-Tibetan Banner paintings (thang-ka) Private collection	C. M. Groen (Mehra, 1970) (p) micr. (ident. as chalk)
late 18th C	Indian 2 polychrome wood sculptures National Museum, New Delhi	O. P. Agrawal (1971) (p) micr. (ident. as chalk)
Gofun (Shell Wh	nite) on Japanese Works of Art	
late 16th to mid-19th C	Japan Ukiyo-e 123 paintings on paper and silk Freer Gallery of Art	E. W. FitzHugh and R. J. Gettens (1979) (p)

⁽p) The calcium carbonate occurs in the paint film proper. In other instances mentioned in these tables, the calcium carbonate has been identified in the ground or preparation of the object concerned (g).

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